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ELECTRONIC MEASUREMENT OF ROCK STRESS

John C. Cook

Teledyne Geotech

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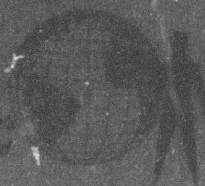
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TDY-20-TR 73-7

FINAL REPORT

ON

ELECTRONIC MEASUREMENT OF ROCK STRESS

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13. ABSTRACT The objective of the program was to evaluate feasibility of non-destructive electronic measurement (and logging) of rock stress in situ, utilizing atomic resonances that are pressure-sensitive. Nuclear quadrupole resonance (NQR) appeared clearly applicable, since no magnetic aligning field is needed, there are several common NQR-active nuclear species in major rock-forming minerals, and rf magnetic fields between 0.3 and 3 megahertz (the resonant frequencies) propagate well through many rocks. There are also alternative resonance methods which may be applicable, including NMR, EPR, and EFR. A comprehensive literature search has been completed on NQR in minerals, which shows that aluminum-27 and a few other elements in feldspars are promising for NQR measurement of rock stress. Efforts to detect these resonances in mineral specimens were mostly unsuccessful because of their extreme weakness. The outlook for NQR is now considered marginal. Short studies of other rf spectrographic methods showed that ferromagnetic effects cannot be used, but that electron paramagnetic resonance (EPR) holds some promise as a means of measuring rock stress, since strong EPR signals are readily obtained from most rocks.			

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to

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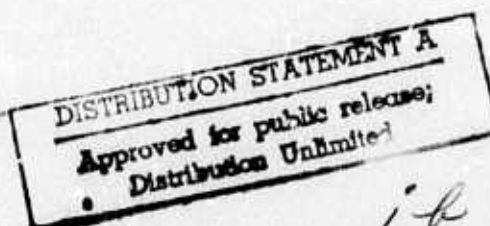
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GLOSSARY

NQR	=	Nuclear quadrupole resonance
NMR	=	Nuclear magnetic resonance
EPR	=	Electron paramagnetic resonance
ZNR	=	Zero field nuclear magnetic resonance
rf	=	Radio frequency
^{27}Al	=	Aluminum-27
^{17}O	=	Oxygen-17
^{35}Cl	=	Chlorine-35
^2H	=	Deuterium-2
^{57}Fe	=	Iron-57
^{55}Mn	=	Manganese-55
^{23}Na	=	Sodium-23
^{39}K	=	Potassium-39

SUMMARY ABSTRACT

A desk and laboratory study has been undertaken, to determine the feasibility of measuring (and logging) rock stress in situ, by nondestructive electronic means employing atomic resonances sensitive to external pressure. A comprehensive literature search and study showed that a large amount of research had been done on electronic (radio frequency) spectroscopic methods, particularly NMR, EPR and "pure" NQR. Nevertheless, most of this work had been devoted to synthetic and organic substances; many of the facts required on mineral resonances for rock stress measurement had not been gathered. An extensive experimental effort was performed, both in company laboratories and in outside institutions. It has now been shown that the only NQR signals of possible value are those of aluminum, sodium, and potassium in the feldspars; but these are so weak that their applicability to rock stress measurement is in doubt. Resonances of ferromagnetic minerals are not usable. The NMR process still has possibilities, but will be difficult to apply. However, EPR effects are strong and widespread in minerals. The outlook for their eventual application to measuring rock stress is considered reasonably good. Further investigation of the EPR method is recommended.

V

ELECTRONIC MEASUREMENT OF ROCK STRESS

1. INTRODUCTION

The purpose of this study was to determine the feasibility of measuring rock stress in situ by purely electronic, non-destructive means. Such a capability might permit rapid measuring of the state of stress in the rock at the exposed surfaces of an underground shaft, drift or tunnel, as well as continuous logging of rock stress in deep drill holes.

The phenomena to be exploited were atomic magnetic resonances at radio frequencies. RF fields introduced at a rock surface can penetrate to substantial depths, of the order of meters to hundreds of meters in most rocks (see Appendix 1). They may thereby couple electromagnetically with multitudes of resonant particles in the rock, which comprise natural stress transducers. The variety of atomic resonance of greatest potential value for this purpose was considered to be "pure nuclear quadrupole resonance" or NQR, which is applicable to many naturally-occurring nuclear species and does not require any magnetic aligning field. Other possible varieties were nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and zero-field nuclear magnetic resonance (ZNR), the first 2 employing the earth's magnetic field (which generally has the required high degree of uniformity), or an artificial field of up to a few hundred oersteds, applied by loops or solenoids carrying direct current, to align the particles. These types of resonance are all applicable to solid compounds and are affected by distortions of the crystal lattice, hence by the absolute mechanical stresses. The resonant frequencies, and/or absorption line widths, and/or line strengths were expected to serve as indicators of stress in a rock. The resonance response of each rock type to stress would be determined by a "calibration:" applying known stresses to a core sample in the laboratory while measuring the resonances, to permit interpretation of the field measurements.

The history of the idea of measuring rock stress with atomic resonances apparently began with Mr. O. K. Kowallis, a former Teledyne employee, who outlined it in an internal company report (Kowallis, 1968). One earlier element of the idea was Benedek's (1965) article on pressure effects in iron. In the absence of the "rock calibration" idea mentioned above, Kowallis reasoned that only a nuclear effect such as NMR could be used. Furthermore, he needlessly ruled out the possibility of using the earth's magnetic field or an applied field for particle alignment, hence confined his attention to NMR of the ferromagnetic materials having strong internal fields, particularly compounds of iron, since ^{57}Fe has a magnetic moment and has a Larmor resonance at what he considered an appropriate frequency (near 45.5 MHz) in pure iron granules. Kowallis recommended that the 62.1 MHz resonance he calculated for magnetite be confirmed (recognizing that this mineral is widely distributed in nature), and predicted that under uniaxial stress, the ^{57}Fe resonance line would be split into two. From data by Benedek (1965) he estimated a pressure effect in iron of $\Delta f/\Delta p = 0.52 \text{ Hz/psi}$, which should permit measurement of pressures by means of frequency to a precision of the order of 200 psi in favorable instances.

With modest company support, Kowallis was able to detect the ^{57}Fe resonance of pure (carbonyl) iron powder at 45.4686 MHz with a volume concentration of iron as low as 1%, using a superregenerative spectrometer. He also detected a resonance in an Ottawa sand sample at 45.250228 MHz, but could not find the predicted 62.1 MHz resonance of magnetite, nor any resonances in several other soils and rocks.

Mr. Kowallis' report was subsequently studied at the Canadian Department of Energy, Mines and Resources in Ottawa, and a detailed report was issued (Gray, 1968). This report pointed out that the Ottawa sand resonance should not arise from the 0.02% of Fe_2O_3 in the St. Peter sandstone of Illinois and its derivatives, including Ottawa sand. Instead, it was suggested that this resonance could be a zero-field ("pure") nuclear quadrupole resonance (NQR) of the oxygen-17 comprising 0.019% of the sand, or that of the aluminum-27 comprising 0.03% of the sand. This suggestion was based on the much stronger magnetic moments of these nuclei as well as their greater abundance compared to the 0.0003% of ^{57}Fe in Ottawa sand; no comparable data were available on the strength of NQR signals from quartz (^{17}O) and corundum (^{27}Al) at the time. Gray (1968) also noted that uniaxial stress would broaden and weaken resonance lines, rather than split them, that each rock might require "calibration" with pressure in the laboratory, and that borehole signals should become strongest when the hole was pressurized to the undisturbed stress level of the rock.

On the basis of Kowallis' work and Gray's recommendations, Teledyne Geotech proposed to ARPA in 1971 to extend their research, as the basis of a possible tool to aid in the Rapid Excavation program. Because of a recognized need for better rock-stress measuring methods, the present program of research was supported despite the expectation by some in the Government that the probability of success was less than 50%.

The program has been concentrated almost entirely upon pure nuclear quadrupole resonance (NQR).

Practically all our results have been negative; we conclude that stress measurements in common types of rock in the field by NQR are not feasible at this time. However, the possibility remains open with regard to certain rocks, if electron paramagnetic resonance (EPR) or NMR of selected minerals is employed. Further research on these methods should be performed.

The following sections summarize the results of a very thorough literature search (covering over one million papers in physics and chemistry published since 1950), and study (of about 200 selected papers), NQR experiments in the most advanced equipments available today, and other experiments of a more preliminary character in NMR and EPR.

2. PURE NUCLEAR QUADRUPOLE RESONANCE (NQR)

2.1 BASIC PRINCIPLES

Good summaries of NQR principles are given in numerous review papers. Possibly the best are the monograph by Das and Hahn (1958) and the recent summary

chapter by Schempp and Bray (1970). For our purposes, a very simple qualitative outline will suffice.

The nuclei of certain atoms behave as if their electric charge were unevenly distributed, over either a prolate or oblate spheroid instead of a sphere. The symmetry axis of the spheroid is also the spin axis, as shown in figure 1. The "protruding" parts are + with respect to the intermediate areas of the nucleus, so the result is a square electric quadrupole: $\begin{smallmatrix} + & + \\ - & - \end{smallmatrix}$, which will experience a torque in the presence of an electric-field gradient. Such gradients are produced around the nucleus by the orbital electrons of the atom, and by charged particles in other surrounding atoms of the crystal lattice. Hence, in crystalline solids there is a definite, built-in aligning field, and the spinning quadrupolar nucleus will precess around it at a characteristic Larmor frequency. If an alternating magnetic field of the same frequency is applied to the crystal by an external coil, enormous numbers of identical "NQR-tuned" nuclei can absorb energy from it, thus affecting the impedance of the coil in a measurable way.

The rules of quantum mechanics govern the entire process. Only nuclei with "spin numbers" I of 1 or greater have an electric quadrupole moment. Energy absorption occurs through quantum transitions. The resonance frequencies ν are determined in simple cases by the magnitude of the nuclear quadrupole moment eQ , measured in (esu)cm², the field gradient eq in (esu)cm⁻², and the quantum numbers I and m , as follows:

$$\nu = (E_1 - E_2)/h = \left[\frac{e^2 q Q}{h} \right] (B_1 - B_2) \quad (1)$$

$$\text{where} \quad B_1 = \frac{3m_1^2 - I(I+1)}{4I(2I-1)} \quad (2)$$

Between the two energy levels E_1 and E_2 , the quantum number m_1 must change by unity. The expression in brackets in (1) is a coefficient that is characteristic of the substance, called the Nuclear Quadrupole Coupling Constant (NQCC). It is determined by experiment, or in favorable cases it can be found by elaborate calculations if Q is known. In many substances, the tensor q is not isotropic, and equation (1) becomes inaccurate. Table 1 lists approximate equations that may be used to find the resonance frequencies ν , providing the gradient-asymmetry parameter η is not too large (from 0 to 0.3, perhaps). Spin numbers I to be used for various nuclear species are given in table 2. Values of the Nuclear Quadrupole Coupling Constant, in megahertz, and of the parameter η for some substances of interest will be given later in table 4.

Since the field gradient q depends on the distances of the charges in adjacent atoms, it is sensitive to changes in the volume of the crystal. Hence, the NQR frequencies are temperature and pressure-sensitive. The latter is the phenomenon we hope to exploit for the electronic measurement of absolute stresses on rocks in situ.

Table 1. Transition frequencies between quadrupole energy levels
(from Biryukov, et al, 1969)

Nuclear spin I	Transi- tion	Frequencies
1	$+1 \rightleftharpoons 0$	$\nu_+ = \frac{3e^2qQ}{4h} \left(1 + \frac{\eta}{3}\right)$
	$0 \rightleftharpoons -1$	$\nu_- = \frac{3e^2qQ}{4h} \left(1 - \frac{\eta}{3}\right)$
3	$+1 \rightleftharpoons 0$	$\nu_1 = \frac{e^2qQ}{20h} (1 + 2\eta + 1.4583\eta^2 - 0.0521\eta^3 - 0.7020\eta^4)$
	$-1 \rightleftharpoons 0$	$\nu_2 = \frac{e^2qQ}{20h} (1 - 2\eta + 1.4583\eta^2 + 0.0521\eta^3 - 0.7020\eta^4)$
	$+2 \rightleftharpoons +1$	$\nu_3 = \frac{e^2qQ}{20h} (3 - 2\eta + 0.2083\eta^2 + 0.0521\eta^3 + 0.0076\eta^4)$
	$-2 \rightleftharpoons -1$	$\nu_4 = \frac{e^2qQ}{20h} (3 + 2\eta + 1.8750\eta^2 - 0.0521\eta^3 - 0.6868\eta^4)$
	$+3 \rightleftharpoons +2$	$\nu_5 = \frac{e^2qQ}{20h} (5 + 0.2083\eta^2 + 0.0521\eta^3 + 0.0076\eta^4)$
	$-3 \rightleftharpoons -2$	$\nu_6 = \frac{e^2qQ}{20h} (5 - 1.4583\eta^2 - 0.0521\eta^3 + 0.7020\eta^4)$
3/2	$3/2 \rightleftharpoons 1/2$	$\nu = \frac{e^2qQ}{2h} \left(1 + \frac{\eta^2}{3}\right)^{1/2}$
5/2	$1/2 \rightleftharpoons 3/2$	$\nu_1 = \frac{3e^2qQ}{20h} (1 + 1.0926\eta^2 - 0.6340\eta^4)$
	$3/2 \rightleftharpoons 5/2$	$\nu_2 = \frac{6e^2qQ}{20h} (1 - 0.2037\eta^2 + 0.1622\eta^4)$
7/2	$1/2 \rightleftharpoons 3/2$	$\nu_1 = \frac{e^2qQ}{14h} (1 + 3.6333\eta^2 - 7.2607\eta^4)$
	$3/2 \rightleftharpoons 5/2$	$\nu_2 = \frac{2e^2qQ}{14h} (1 - 0.5667\eta^2 + 1.8595\eta^4)$
	$5/2 \rightleftharpoons 7/2$	$\nu_3 = \frac{3e^2qQ}{14h} (1 - 0.1000\eta^2 - 0.0180\eta^4)$
9/2	$1/2 \rightleftharpoons 3/2$	$\nu_1 = \frac{e^2qQ}{24h} (1 + 9.0333\eta^2 - 45.6910\eta^4)$
	$3/2 \rightleftharpoons 5/2$	$\nu_2 = \frac{2e^2qQ}{24h} (1 - 1.3381\eta^2 + 11.7224\eta^4)$
	$5/2 \rightleftharpoons 7/2$	$\nu_3 = \frac{3e^2qQ}{24h} (1 - 0.1857\eta^2 - 0.1233\eta^4)$
	$7/2 \rightleftharpoons 9/2$	$\nu_4 = \frac{4e^2qQ}{24h} (1 - 0.0809\eta^2 - 0.0043\eta^4)$

Table 2. Characteristics of the stable isotopes of nuclei of spin $I \geq 1$
(from Biryukov, et al, 1969)

Element	Atomic number	Mass number	Natural abundance, %	Nuclear spin I	Magnetic moment, nuclear magnetons	Magnetogyric ratio, $\text{Hz} \cdot \text{gauss}^{-1}$	Quadrupole moment, $Q \cdot 10^{-24} \text{ cm}^2$	Quadrupole moment ratio
D	1	2	0.0156	1	0.85738	653.5	0.00277	
Li	3	6	7.43	1	0.82191	626.5	0.00046	$Q_6/Q_7 =$ $= 0.019$
		7	92.57	3/2	3.2559	1654.7	-0.042	
Be	4	9	100	3/2	-1.1774	598.3	0.02	
B	5	10	18.83	3	1.8006	457.5	0.074	$Q_{10}/Q_{11} =$ $= 2.084$
		11	81.17	3/2	2.6880	1366	0.0355	
N	7	14	99.635	1	0.40357	307.6	0.02	
O	8	17	0.037	5/2	-1.8930	577.2	-0.026	
Na	11	23	100	3/2	2.2161	1126.2	0.1	
Mg	12	25	10.05	5/2	-0.85471	260.6		
Al	13	27	100	5/2	3.6385	1109.4	0.149	
S	16	33	0.74	3/2	0.64274	326.6	-0.064	
Cl	17	35	75.4	3/2	0.82089	417.2	-0.0797	$Q_{35}/Q_{37} =$ $= 1.2688$
		37	24.6	3/2	0.88329	347.2	-0.0621	
K	19	39	93.08	3/2	0.39094	198.7	0.09	$Q_{39}/Q_{41} =$ $= 1.220$
		41	6.91	3/2	0.21453	109.2	0.11	
Ca	20	43	0.13	7/2	-1.3153	286.5		
Sc	21	45	100	7/2	4.7491	1034.3		
Ti	22	47	7.75	5/2	-0.7871	240.0		
		49	5.51	7/2	-1.1023	240.1		
V	23	51	100	7/2	5.1392	1119.3	0.3	
Cr	24	53	9.5	3/2	-0.4735	240.6		
Mn	25	55	100	5/2	3.4610	1055.3	0.5	
Co	27	59	100	7/2	4.6388	1010.3	0.5	
Cu	29	63	69.1	3/2	2.2206	1128.5	0.15	$Q_{63}/Q_{65} =$ $= 1.0806$
		65	30.9	3/2	2.3790	1209	-0.14	
Ga	31	69	60.2	3/2	2.0108	1021.8	0.19	$Q_{69}/Q_{71} =$ $= 1.5867$
		71	39.8	3/2	2.5549	1298.4	0.12	
Ge	32	73	7.61	9/2	-0.8768	148.5	-0.2	
As	33	75	100	3/2	1.4349	729.2	0.3	
Br	35	79	50.6	3/2	2.0990	1066.7	0.33	$Q_{79}/Q_{81} =$ $= 1.1970$
		81	49.4	3/2	2.2626	1149.8	0.28	
Kr	36	83	11.55	9/2	-0.968	164	0.22	
Rb	37	85	72.8	5/2	1.3483	411.1	0.3	$Q_{85}/Q_{87} =$ $= 2.07$
		87	27.2	3/2	2.7415	1393.2	0.15	

Table 2, (Continued)

Element	Atomic number	Mass number	Natural abundance, %	Nuclear spin I	Magnetic moment, nuclear magnetons	Magnetogyric ratio, Hz · gauss ⁻¹	Quadrupole moment, Q · 10 ⁻²⁴ cm ²	Quadrupole moment ratio
Sr	38	87	7.02	9/2	-1.0893	184.5		
Nb	41	93	100	9/2	6.1435	1046.7	-0.2	
Mo	42	95	15.78	5/2	-0.9099	277.4		
		97	9.60	5/2	-0.9290	283.3		
Pl	46	105	22.23	5/2	-0.57	174		
In	49	113	4.16	9/2	5.4960	931.0	1.144	$Q_{115}/Q_{113} =$
		115	95.84	9/2	5.5072	932.9	1.161	$= 1.0146$
Sb	51	121	57.25	5/2	3.3417	1019	-0.53	$Q_{123}/Q_{121} =$
		123	42.75	7/2	2.5334	551.8	-0.68	$= 1.27475$
I	53	127	100	5/2	2.7939	851.9	-0.88	
Xe	54	131	21.24	3/2	0.6868	349	-0.12	
Cs	55	133	100	7/2	2.5642	558.5	-0.003	
Ba	56	135	6.6	3/2	0.837	425		$Q_{137}/Q_{135} =$
		137	11.3	3/2	0.936	476		$= 1.542$
La	57	139	99.911	7/2	2.7615	601.4	0.5	
Pr	59	141	100	5/2	3.8	1130	-0.054	
Nd	60	143	12.2	7/2	-1.1	220	≤ 1.2	
		145	8.3	7/2	-0.69	140	≤ 1.2	
Sm	62	147	15.07	7/2	-0.68	147	0.72	
		149	13.84	7/2	-0.55	119	0.72	
Eu	63	151	47.8	5/2	3.4	1000	~ 1.2	
		153	52.2	5/2	1.5	460	~ 2.5	
Yb	70	173	16.08	5/2	-0.65	198	3.9	
Lu	71	175	97.4	7/2	2.6	570	5.9	
Ta	73	181	100	7/2	2.1	460	3.9	
Re	75	185	37.1	5/2	3.1437	958.6	2.8	$Q_{185}/Q_{187} =$
		187	62.9	5/2	3.1760	968.4	2.6	$= 1.06$
Os	76	189	16.1	3/2	0.6507	330.7	0.8	
Ir	77	191	38.5	3/2	0.16	81	1.5	
		193	61.5	3/2	0.17	86	1.5	
Au	79	197	100	3/2	0.136	69.1	0.56	
Hg	80	201	13.24	3/2	-0.607	308	0.5	
Bi	83	209	100	9/2	4.0389	684.3	-0.4	

2.2 GEOCHEMICAL CONSIDERATIONS

A substantial proportion of natural nuclides exhibit NQR. These are listed in table 2, which was taken from the recent comprehensive book by Biryukov, et al (1969). Most of these are relatively rare in the earth's crust, but a few are among the petrogenic or "lithophilic" elements found in quantity in igneous rocks (Rankama and Sahama, 1950) as summarized in table 3.

Table 3. The most abundant NQR-active isotopes

<u>Lithophilic element</u>	<u>Percent in igneous rocks</u>	<u>NQR isotope</u>	<u>Abundance, percent</u>	<u>Isotopic abundance in igneous rocks</u>
Aluminum	8.13%	^{27}Al	100%	8.13%
Sodium	2.8%	^{23}Na	100%	2.8%
Potassium	2.59%	^{39}K	93.4%	2.43%
Magnesium	2.09%	^{25}Mg	11.5%	0.24%
Potassium	2.59%	^{41}K	6.6%	0.17%
Manganese	0.1%	^{55}Mn	100%	0.1%
Oxygen	46.6%	^{17}O	0.041%	0.019%
Calcium	3.63%	^{43}Ca	0.15%	0.005%

Others below 0.1% isotopic abundance: ^{47}Ti , ^{35}Cl , ^{11}p .

The nuclides below the broken line in table 3 may not be as high in isotopic abundance (igneous rocks) as some of the minor elements, but are the only important NQR-active constituents of major sedimentary rocks such as sandstone, limestone and evaporites.

It is unfortunate that the most abundant rock-forming elements, oxygen 16 and silicon, as well as carbon, are not NQR-active.

The most abundant minerals in igneous rocks, according to several authorities (Rankama and Sahama, 1950), are the following:

Feldspars - 59.5% to 67.5%
 Quartz - 9% to 17.6%
 Mg, Fe, Ca silicates (hornblende, pyroxenes, micas) - 12 to 20%
 Ilmenite - 1% to 2%
 Apatite - 0.4% to 0.7%.

Clearly, the aluminum present in all feldspars, $\text{K,Na(AlSi}_3\text{O}_8)$ or $\text{Ca,Ba(Al}_2\text{Si}_2\text{O}_8)$, offers the best possibility as an NQR-active element widespread in natural rocks. Secondary possibilities exist with the sodium and potassium also

present in many feldspars. Fortunately, nuclear quadrupole coupling constants have been measured in two feldspars, albite and microcline, as a by-product of NMR measurements (Hafner and Hartmann, 1962). These are listed in table 4, together with those of all the other reasonably abundant minerals for which data have been found in a very thorough literature search. Unfortunately, most NQR work in minerals has been done on gem-quality semi-precious stones, or on relatively rare minerals of arsenic, bismuth, or copper.

2.3 OTHER RESULTS FROM THE LITERATURE STUDY

Most of the basic quadrupolar parameters for minerals listed in table 4 were obtained from experiments other than pure nuclear quadrupole resonance. Hence, for guidance in our experiments, it has been necessary to calculate most of the expected resonance frequencies shown, using the formulas of table 1. These frequencies provide a guide for laboratory searches for the resonances, although discrepancies of up to ± 10 percent are expected to be found. Some errors arise from the inexactness of the formulas of table 1 where η is large, others from variations of the parameters with temperature, (the NQCC generally decreases at higher temperature), and still others from variations caused by dispersed impurities, which locally distort the crystal lattice slightly (Schempp and Bray, 1970) and vary among different samples.

It will be noticed in table 4 that there are at least two resonances for ^{27}Al in each mineral, and there may be many more (Kyanite has 8). The same is true of ^{17}O . The feldspars and other simple alumino-silicates have all their ^{27}Al pure quadrupole resonances between about 300 kilohertz and 1 megahertz. The ^{17}O resonances between 1.47 and 5.36 MHz for ice and Al_2O_3 suggest that if the oxygen resonance can be observed in quartz, it will be found in this general vicinity, or possibly up to 13 MHz (Lucken, 1969). No published NQR data for ^{17}O in quartz were found, despite extensive searching. Sodium-23 and potassium-39 resonances may also be found in this range or lower (Lucken, 1969), judging from the meager data available.

These frequencies are generally considered "too low for convenient study" (Schempp and Bray, 1970). This is probably because the absorption line widths and separations are an appreciable fraction of the center frequency. The instrument most favored in this frequency range is the marginal oscillator, with frequency modulation. However, "FM has not been successful where the lines are very broad" (Schempp and Bray, 1970). Data on mineral resonance line widths are sparse and scattered. Marfunin (1965) states that the NQR signal amplitude is proportional to: (resonance frequency/line width), with the usual stationary detection methods. This means that the detectability of the lines depends greatly on the rarity and crystal perfection of the specimen. For this reason, most NQR studies of minerals have employed optically clear, semi-precious stones. Cloudy specimens have not given NQR lines. However, Marfunin (1965) points out that pulsating techniques are not subject to the line-width limitation on amplitude, and that by their use NQR's can be observed in crystals where they would be otherwise undetectable (also see Smith, 1971). One sophisticated example is the experiment of Slusher and Hahn (1964), in which ^{23}Na , ^{35}Cl , and ^{37}Cl pure quadrupole resonances were detected by a special pulse technique in salt, NaCl , despite up to 0.2 percent of lattice impurities and otherwise cubic symmetry.

Table 4. Summary of selected mineral NQR data

Isotope	I	Mineral	NQCC		Resonances, MHz	Reference
			(e ² Qq/h), MHz	n		
²⁷ Al	5/2	Albite	3.29, <u>3.37</u>	0.62, <u>0.634</u>	(0.655), (0.932)	i
"	"	Microcline	3.22	0.21	(0.506), (0.956)	l
"	"	Spinel	3.72	0	(0.556), (1.12)	j
"	"	Topaz	1.55, 1.67	0.8, 0.38	(0.334), (0.287) (0.434), (0.488)	a, b
"	"	Corundum	2.393	0	0.359, 0.718	c
"	"	Spodumene	2.950	0.94	0.751, 0.793	d
"	"	Beryl	3.093	0	0.464, 0.927	d
"	"	Chrysoberyl	2.85, 2.846	0.94, 0.76	(0.63), (0.605) (0.81), (0.80)	e
"	"	Kyanite	3.7, 6.5	0.89, 0.59	(0.812), (1.27) (1.045), (1.85)	f
"	"	"	9.4, 10.0	0.38, 0.27	(1.43), (1.62) (2.74), (2.96)	f
"	"	Andalusite	5.9, 15.6	0.69, 0.08	(1.22), (2.32) (1.66), (4.65)	f
"	"	Al (metal)	<0.63	-	<0.94, <0.188	h
¹⁷ O	"	H ₂ O (gas, ice)	9.83, 6.66	0.4, 0.93	(1.71), (1.47) (2.86), (1.89)	i, g, k
"	"	Corundum	18.9	0.62	(3.76), (5.36)	m
²³ Na	3/2	Albite	2.64, <u>2.62</u>	0.25	(1.29)	l
²³ Na	"	NaCl (gas)	5.40	-	(2.70)	g
³⁹ K	"	KCl (gas)	5.67	-	(2.83)	g
³⁵ Cl	"	AlCl (gas)	8.8	-	(4.4)	g
² H	1	H ₂ O (gas, ice)	0.318, 0.214	0.06, 0.1	(0.234), (0.155) (0.243), (0.166)	k
⁷ Li	3/2	Spodumene	0.0757	0.79	(0.0417)	d

NOTES:

1. Some crystals have the active isotope at more than one type of site in the unit cell, hence have several values of n and NQCC.
2. Underlined values are alternatives, given in secondary references.
3. Parentheses denote my calculation, from data given.

Pen'kov and Sofin (1967) say that the intensity of an NQR signal is proportional to (gyromagnetic ratio)² for the active nucleus. As can be seen in table 2, ²⁷Al, ²³Na and ⁷Li have large gyromagnetic ratios, and should give NQR signals 7 to 16 times as large as ³⁵Cl, which is one of the most popular and easily detected isotopes. This is encouraging. The signals from ¹⁷O, ³⁹K, and ²H should be more nearly comparable to that from ³⁵Cl.

Pressure applied to a crystal generally increases the NQCC and the resonant frequencies (Schempp and Bray, 1970). It may also reduce the signal amplitude. The magnitude of the pressure coefficient appears to depend upon the compressibility, the degree of covalent bonding, and the volume dependence of thermal vibrations in the crystal. The papers of Kushida et al, Armstrong and Jeffrey, Early et al, and D'Alessio and Scott listed in part II-C of appendix 2 discuss the details. Near room temperature, some typical pressure coefficients of frequency $\partial\nu/\partial P$ are:

for ³⁵Cl in KClO₃, +0.46 Hz/psi for $\nu = 28$ MHz.
for ⁶³Cu in Cu₂O, + 2.47 Hz/psi for $\nu = 26$ MHz.
for ²³Na in NaNO₃, - 0.33 Hz/psi for $\nu = 0.16$ MHz.

In the last-named, the coefficient becomes zero at about 200°C and positive above that temperature.

There is a Zeeman splitting and weakening effect on NQR lines by external magnetic fields. This effect can be used to modulate, and thus identify, NQR absorptions, with advantages in stability over frequency modulation, the technique generally used in steady-state NQR work (Smith, 1971).

Powdered or polycrystalline samples appear to be generally satisfactory for NQR, except in ductile (metallic) materials in which cold-working residual strains may be created. However, "surface defects" may cause weak spurious signals in finely powdered samples (Slusher and Hahn, 1964). Annealing should be done in vacuum to prevent absorption of gaseous impurities from the atmosphere. Thermal annealing at temperatures approaching melting can improve the NQR signal in some materials; in others a partial phase transition apparently occurs which introduces much disorder in the crystal and destroys the signal (Brun, Hafner and Hartmann, 1960). Hence, de-stressing of minerals by crushing appears to be preferable to heating, if it should be required.

2.4 FIRST NQR EXPERIMENTS

The experiments began with a practical search for pure nuclear quadrupole resonances in common rock-forming minerals. A marginal-oscillator-type cw spectrometer built in 1969 at Teledyne Geotech for NQR studies of nitrogen compounds (Cook, 1970) was restored to operation and several improvements were added. The oscillator and buffer amplifier circuit used, taken from Gill et al (1967), is shown in figure 2. It was followed by a conventional audio band-pass amplifier (Gill et al, 1967, figure 2) passing about 500 to 1500 Hz. The output was displayed on an oscilloscope, whose sweep was line-synchronized. The Varicap frequency modulator was driven at 60 Hz by a 6.3 v filament transformer. A 50 MHz frequency counter driven by the E180F rf buffer was used to measure frequencies. Oscillator harmonics and waveforms

were monitored with a communications receiver and a 50 MHz oscilloscope. Interchangeable rf tank coils were provided having from 1 turn to 60 turns of 2-1/4 inches inside diameter, to tune from 1.5 to 58 MHz with the 100-100 pfd twin variable tuning condensers. Unfortunately, this circuit would not oscillate from about 4 to 10 MHz, despite several kinds of feedback adjustments. Oscillation above this gap was of low amplitude and apparently occurred in a different mode.

The equipment was checked, as in 1969, with a sample of hexamethylene tetramine $(\text{CH}_2)_6 \text{N}_4$, whose nitrogen-14 resonances near 3.3 MHz were easily detected. In pure samples, only one resonance is supposed to occur. Our commercial-grade (Eastman) sample, however, probably contains homologous, slightly different compounds, since we have always observed more than a dozen closely-spaced absorption "lines." The spectrometer was found to be working and adjustments were made for strongest signals.

Samples of Ottawa sand were obtained from a local cement manufacturer. This sand, used as a laboratory standard, is quarried in Ottawa, Illinois. Instead of the resonance at 45.25 MHz in this sand reported by O. K. Kowallis (1967), we observed a group of absorption lines just below 22 MHz, and none near 45 MHz. This may indicate that the resonance found by Kowallis was really at 22.62 MHz, and that the frequency was misread in his experiment because of a prominent second harmonic from the oscillator. Attempts were made to find these 22 MHz resonances in large crystalline quartz specimens from Brazil and from Arkansas, without success. This result, together with the likelihood that ^{17}O nuclear quadrupole resonances in other simple compounds occur below 1 MHz (table 4), indicates that the resonance in the Ottawa sand is an EPR or EFR impurity resonance, and does not arise from the oxygen-17 component of the quartz.

An attempt was made to remove the impurity-carrying grains from the Ottawa sand by "combing" it with a strong magnet. Some grains were thus removed, but the remaining sand still gave the resonances, and the separated fraction did so only in the same proportion to its volume as the original sample. It was concluded that the resonances were not caused by separate, palpable grains of magnetite or other ferrimagnetic minerals. A clue to their origin is that of the two grades of Ottawa sand obtained, the coarse #190 gave much stronger signals than the fine #109.

Empirical manual searches for resonances were made between 1.5 and 4 MHz on 1 lb samples, which nearly filled the coils, of clear quartz, clear calcite, opaque ruby (corundum), opaque orthoclase feldspar, and red granite. No strong resonances were found, except spurious ones from the equipment or environment (radio stations).

Upon completion of the literature study, it became clear that most of the pure quadrupole resonances sought should be found below 1 MHz (table 4); also, they probably require a very narrow equipment bandwidth, as provided by very slow automatic frequency scanning and phase detection, to be separated from noise. Hence, the equipment was modified to operate at frequencies down to 0.31 MHz, was fitted with a slow motor-drive for the tuning condensers (10 minutes or 5 hours per scan) and a limit switch. Phase detection, low-pass filtering and strip-chart recording were also added. A block diagram of the final spectrometer is given in figure 3. Systematic searches of the region between

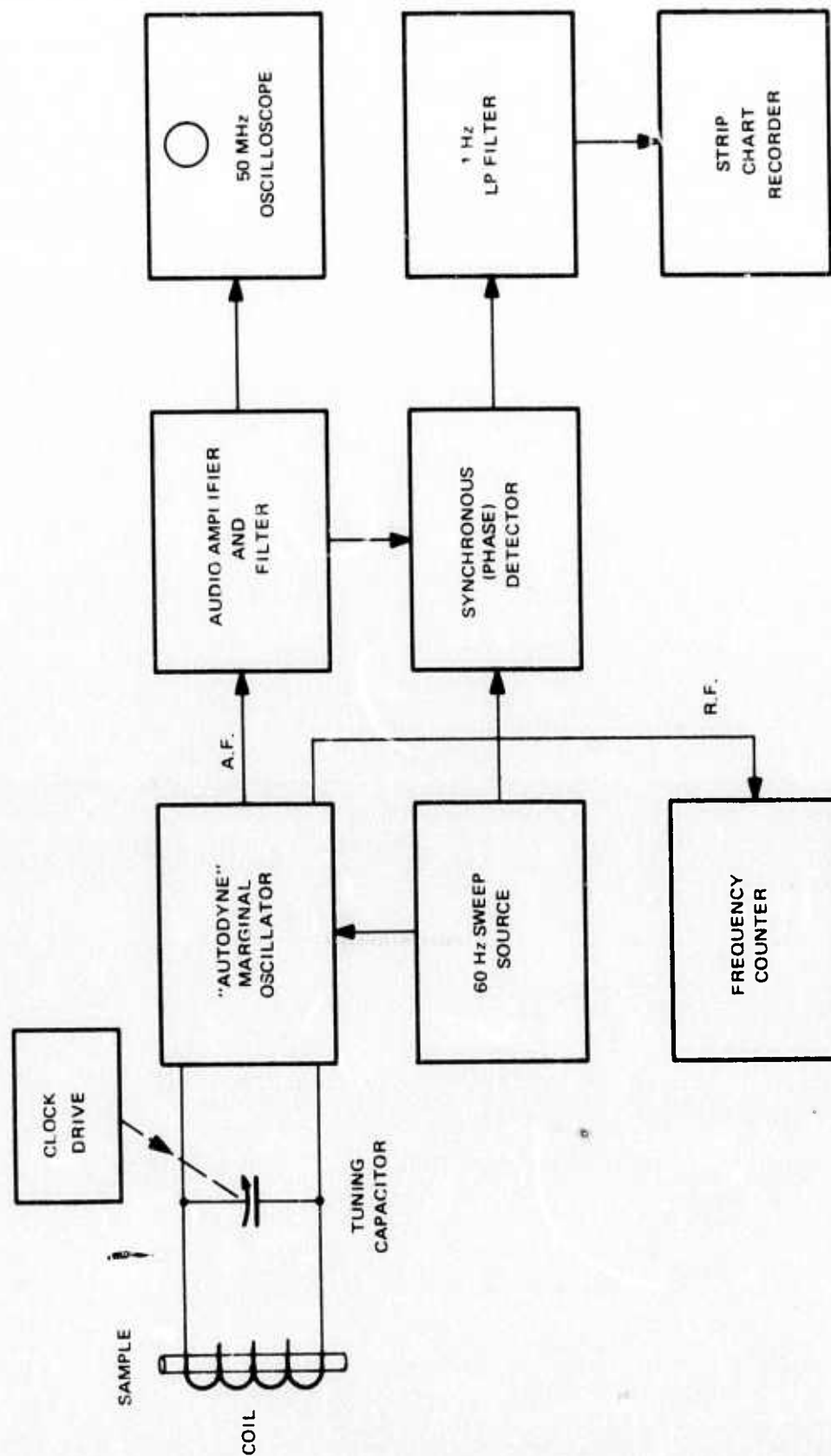


Figure 3. Block diagram of final C.W. spectrometer arrangement

0.44 and 1.2 MHz were made on 1 lb specimens of clear quartz, Madagascar ruby, synthetic ruby and sapphire (all corundum), calcite, and orthoclase feldspar without result. In the course of these searches, many combinations of fm modulation excursion, scan rate, field strength, oscillator stability setting, etc., were made. The second harmonic of the modulation frequency (60 Hz or 400 Hz) was generally used for the best compromise between sensitivity and false amplitude modulation. A small tuned LC circuit could be loosely coupled to the specimen coil in place of the mineral sample for checking the equipment response; its absorption peak was much broader than the lines seen with hexamethylene tetramine, however.

Careful searches were made especially for the two known resonances of ^{27}Al in corundum at 0.359 and 0.718 MHz, as revealed by the splitting of the NMR line of ^{27}Al at high magnetic fields into five components by the quadrupole effect. Nothing was found except spurious apparatus resonances which persisted with the sample removed. (Some of these are attributed to the piezoelectric mica in the vacuum tubes.)

2.5 NQR CONSULTATIONS AND ADVANCED EXPERIMENTS

Our lack of initial success in locating suitable nuclear quadrupole resonances in samples of common rock-forming minerals using a regenerative C.W. spectrometer led us to seek the advice of full-time specialists in NQR. Dr. Thomas A. Scott of the University of Florida, who wrote summaries of worldwide NQR work in 1970 and 1971 for the Magnetic Resonance Review, was contacted first. Through him, other specialists were located. Dr. Scott's C.W. spectrometers, used in studying the structures of nitrogen compounds, were found to be highly-developed devices which had been refined over several years. Such refinement was of course impossible for us to achieve in the present short program. Dr. Scott knew of no NQR work on ^{27}Al or ^{17}O , other than the references already located (see bibliography), but he gave much general advice on NQR technique and the state of the art.

In a visit to Dr. Wm. Moulton at Florida State University, we were advised that pulse spectrometers are far more sensitive than C.W. spectrometers, and were shown a demonstration of the ^{17}Cl resonance in KClO_3 on a recently-designed pulse spectrometer. Dr. Moulton advised us that NQR was a much less promising method of measuring pressure effects in minerals than are EPR (of colored minerals) or EFR (in trace minerals of "magnetically ordered" character such as magnetite). He and his staff emphasized that the scarcity of ^{17}O , which is only 0.037% of all oxygen, the absence of any NQR effect in the really abundant lithophilic elements, and the complexity, variable composition and opaque character of the feldspars and other silicates containing substantial amounts of ^{27}Al , should discourage any attempt to employ NQR methods. Judging from subsequent experience, this advice was correct.

2.5.1 Pulse-Method Searches

Despite Dr. Moulton's advice, we decided to explore fully the quantitative limitations of NQR in rocks, in accordance with contract provisions, because of the broad applicability of a method using ^{17}O or ^{27}Al , and because of the convenience in not having to provide an aligning magnetic field. Arrangements

were made with Dr. Slade Carr of the Florida A & M University to search for resonances in several crushed mineral specimens supplied by us, using an advanced pulse spectrometer. Dr. Carr had a reputation as an expert searcher with this instrument. Unfortunately, it was found incapable of being tuned to frequencies below 2 MHz. Empirical searches were performed from 2 to 4 MHz on a few specimens, and from 4 to 8 MHz on specimens of 13 minerals, including synthetic sapphire and ruby (corundum), natural grey corundum and ruby, quartz, calcite, orthoclase and albite feldspars. Nothing was found.

Arrangements were made with Dr. Tonis Oja at the University of Denver to perform searches on his pulse spectrometer of recent design (figure 4) (Oja, 1972) which was capable of operating at frequencies from 0.50 to 5.4 MHz. Five days of tedious searching by the Principal Investigator and by Dr. Oja yielded no ^{27}Al or ^{17}O resonances from carefully prepared, crushed 50-gram samples of various corundums and feldspars purchased from Linde and from Filer's Mineral Supply Co.

The searches were concentrated around the resonant frequencies given in table 4, at both room temperature and in liquid nitrogen (77°K). The two-pulse method was used, employing a "90 degree" pulse and a "180 degree" pulse as shown in figure 5. The areas of these pulses were carefully adjusted so that the second pulse was just twice the first, which was determined by:

$$t H = \frac{\pi}{\gamma} \sqrt{(I - |m|)(I + |m| + 1)} \quad (3)$$

The pulse length t and field strength H thus depend upon the gyromagnetic ratio γ and spin I of the nucleus being sought (see table 2). The quantum transition number m is 1/2 for the lower frequency and is 3/2 for the upper frequency. Since the r.f. magnetic field strength H could not be measured with the equipment available, it was estimated from the resonance voltage E across the sample coil, which was part of a parallel resonant circuit (figure 4), according to the following formulas:

$$i = E / \sqrt{X^2 + R^2} = E\omega CQ / \sqrt{Q^2 + 1} \doteq E\omega C \quad (4)$$

$$H = Ni/10 L = NE\omega C/10L \quad (5)$$

Here N and L are the total turns and length of the coil, C the tuning capacitance at angular frequency ω , as measured on a Q-meter for each frequency and each coil before installation, and E is the r.f. voltage (peak to peak) as measured across the coil with an oscilloscope. These formulas permitted the correct adjustments of the product tE to be made for each of the several coils required for the various resonance ranges searched. The coil Q 's were all above 100, so that the approximation in formula (4) is permissible. The calculated product tE was checked against optimum values found empirically for nitrogen and niobium compounds which gave good signals in the equipment (with proper compensation for the I , γ and m 's of these elements). It was only necessary to make tE correct to within about a factor of 2.

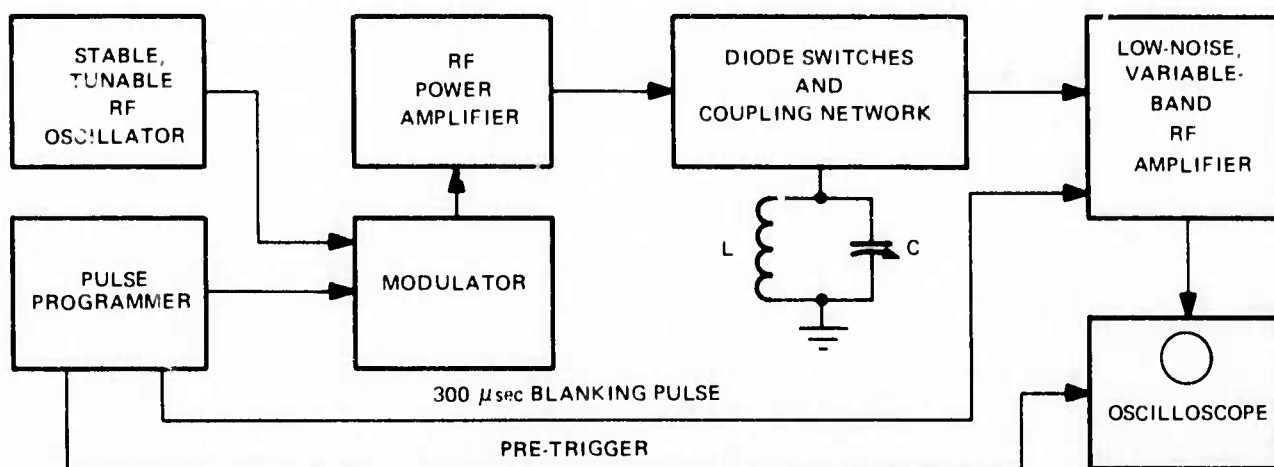


Figure 4. Block diagram of pulsed NQR spectrometer

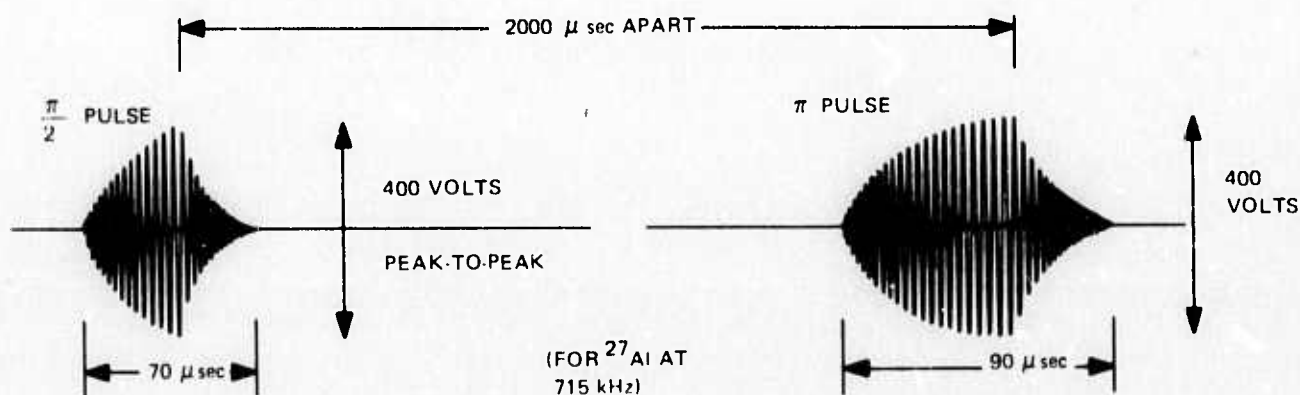


Figure 5. Typical pulse sequence applied to coil

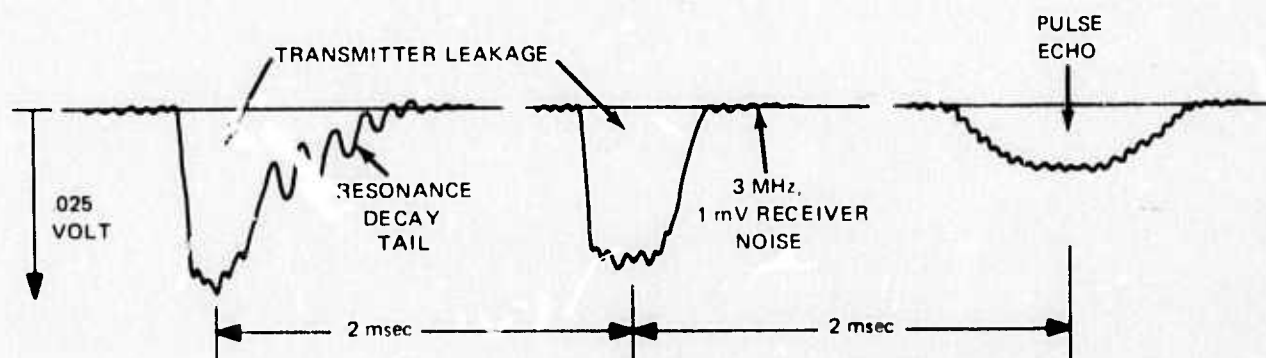


Figure 6. Typical signal sequence expected from receiver

A sealed specimen of aluminum tribromide was also tried in the pulse spectrometer. This specimen had given a strong ^{27}Al NQR signal in a CW spectrometer some years before. No resonances were found by the pulse method. The equipment was rechecked on some nitrogen compounds, with good results; in fact, two new ^{14}N resonances in an organic compound never studied before were discovered by Dr. Oja after about an hour's searching. Figure 6 illustrates the appearance of the "decay tail" and "echo" signals so obtained, which were sought but never seen with specimens containing aluminum.

Because of the possibility of sample "saturation" by the r.f. field, which could rapidly quench the signal, the searching was done with individual pulse-pair events, applied by means of a command pushbutton at intervals of at least 1 second (to allow time for thermalization recovery of the nuclear spin system). Between events, the RF oscillator was generally changed in frequency in 1 kHz steps. About each 10 kHz, several adjustments on the transmitter and coupling network had to be retuned to preserve the tE product and to avoid distortion of the pulses. The best search rate achieved was only 100 kHz per hour. In view of the many variables involved, all the possible combinations could not be thoroughly explored while the equipment was available.

Our failure to find any ^{27}Al resonances was attributed to one or more of the following causes:

- a. All the samples may have been unsuitable, lacking detectable resonances because of strains or impurities.
- b. The values of tE used and the frequency ranges searched were incorrect, despite the best available theoretical guidance and much care in calculating and measuring tE by alternative independent methods.
- c. The spin-lattice relaxation times T_1 for these samples were much longer than 1 second, so that the signals did not appear more than once before saturation occurred, and were discounted as "noise."
- d. The values of T_1 were much shorter than 300 microseconds, the minimum blanking and recovery time possible for the particular receiver; hence, the "decay tail" signal was over before the receiver was working and there was insufficient nuclear coherence to form a pulse echo.

To test hypothesis (d), arrangements were made through Dr. Oja to use a new low-frequency pulse spectrometer of advanced design built by Mr. Gary Peterson, an expert specialist with MATEC, Inc. of Warwick, R. I. This instrument had a receiver "dead time" of only 40 microseconds. It first became available during the January 1973 meeting of the American Physical Society in New York City, where it was being demonstrated. Twelve hours of searching for the ^{27}Al resonances in various corundums and feldspars were done by three MATEC, Inc. experts and by the Principal Investigator. For much of this work a digital transient-memory and display unit was used to enhance observation of the short-lived waveforms displayed. Both room temperature and liquid nitrogen temperature were used. Pulse sequences were applied as much as 30 seconds apart to avoid possible saturation effects. Nevertheless, no resonances were found.

2.5.2 Related NMR Findings

In the meantime, a publication was obtained from Switzerland (Hartmann, 1963) giving details of NMR experiments on natural feldspars, showing that many such minerals can show the quadrupole splitting effect in ^{27}Al quite clearly, as seen in figure 7. After a lengthy series of inquiries, arrangements were made with Dr. Irwin Weisman at the National Bureau of Standards to run NMR spectra of samples furnished by us, to determine if they exhibited quadrupole splitting and thus to test hypothesis (a) above. He immediately found the quadrupole splitting in the Linde synthetic sapphire (figure 8), but only weak hints of splitting in two natural feldspars. A major reason was probably that in the crushed samples furnished, the random crystal orientations smeared the positions of the four satellite lines too much, since their separation from the central peak (figure 7) varies greatly with crystal orientation in the NMR method (Hartmann, 1963) (crystal orientation affects only the amplitude of pure NQR signals, hence crushed samples give a signal about half as large as an optimally-oriented single crystal).

Arrangements could not be made to have Dr. Weisman's initial results extended at the Bureau of Standards, because of administrative difficulties. Attempts were made to test single crystals and additional samples in a standard high-resolution NMR spectrometer at an institution in Texas, without success; its bandwidth and modulation were far too narrow for the wide spectral lines found in solids. Calls to universities and major government and industrial laboratories throughout the nation failed to locate another wide-line NMR spectrometer equipped to operate in the ^{27}Al region (which is near that of carbon-13). However, it was concluded that hypothesis (a) above had been essentially disproven; the synthetic sapphire, at least, should give a pure NQR signal.

2.5.3 Final C.W. Experiments

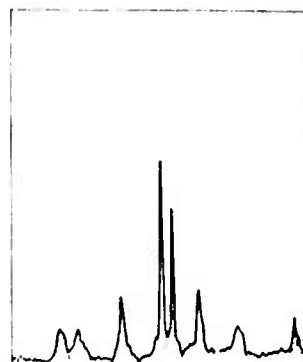
Finally, arrangements were made with Dr. Thomas A. Scott at the University of Florida, for his staff to perform pure NQR searches on some mineral specimens, using his advanced CW equipment with the summation of repeated frequency scans. We reasoned that whatever the errors in adjustment (hypothesis b) or peculiarities of ^{27}Al (hypotheses c and d) which prevented its detection in the pulse experiments, these should not affect the CW method.

After initial difficulties from piezoelectric behavior of the synthetic sapphire, zeeman (magnetic field) modulation was used. Radio station interference was eliminated by careful shielding. Weak resonances were finally found at 0.363 MHz and 0.722 MHz, within 1% of the predicted values. Figure 9 shows the accumulated result of 128 passes through the lower resonance. A comparison recording with the resonance destroyed by an inhomogeneous d.c. magnetic field is also shown. The resonance width is about 7 kHz and the signal-to-noise amplitude ratio is about 2. All tests were made at room temperature.

Samples of an albite from Gunnison, Colorado, and a microcline from Sonora, California, also gave repeatable but very weak signals at frequencies within 3% of the values predicted by table 4. Table 5 below summarizes all results. These results required a week's time to acquire, in a well-equipped laboratory specializing in low-frequency NQR, by skilled experts with years of experience (in particular, Paul Canapa). They are surely representative of the best that can be done at this time.

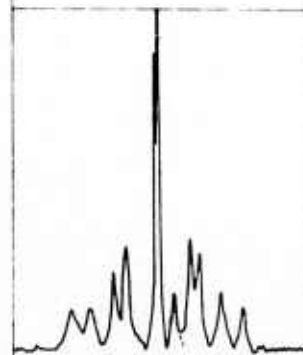
(a) Albite single crystal,
from Amelia Court House, Va.

a)



(b) Twinned polycrystalline
microcline from Crystal
Peak, Colorado

b)



(c) Microcline single crystal
from Hull, Quebec.

c)

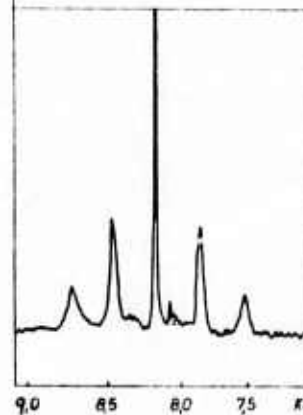


Figure 7. NMR spectra of three feldspars at 9 Mc, with lines from ^{27}Al and ^{23}Na (shaded); from Hartmann (1963). Optimum orientations.

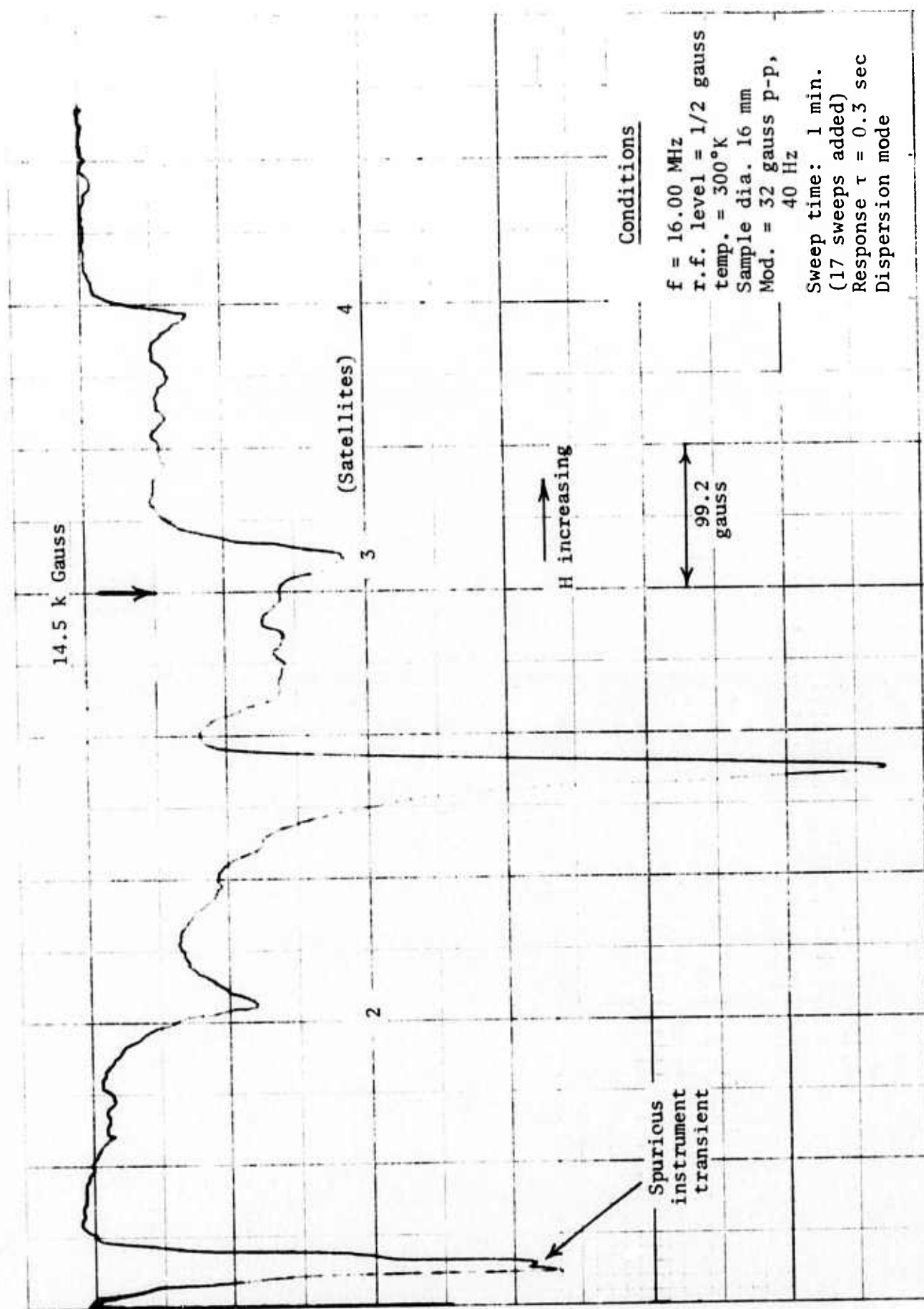


Figure 8. Wide-line NMR spectrometer recording for crushed sapphire

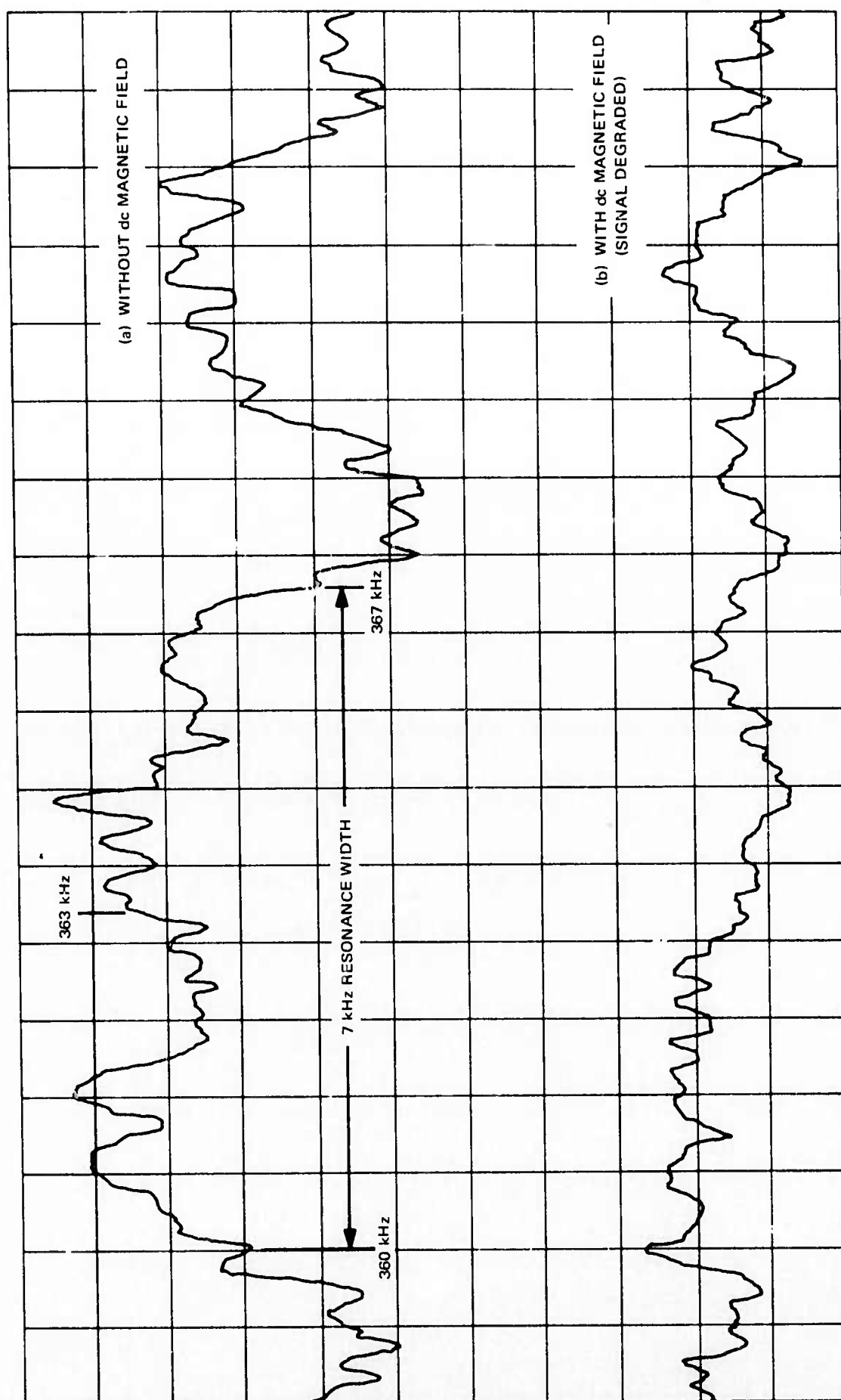


Figure 9. Averaged recording from 128 scans of pure NQR signal from synthetic sapphire

Table 5. C.W. NQR Results

<u>Mineral</u>	<u>No. of scans summed</u>	<u>Frequency, MHz</u>	<u>Line width, MHz</u>	<u>Signal/ noise</u>
Synthetic sapphire	{ 128	0.363	0.007	2
	{ 100?	0.722	0.010	3?
Albite	64	0.955	0.010	1.5(?)
Microcline	156	0.925	0.018	1.5(?)

2.5.4 In Quest of Oxygen-17 NQR Signals

Throughout the early empirical searches with CW and pulse spectrometers, large single-crystal specimens (up to 1 lb) of clear calcite, quartz, and corundum (Linde synthetic sapphire and ruby scrap) were tested repeatedly in the frequency range of 1 to 6 MHz, where pure NQR resonances of ^{17}O can be expected according to table 4. Nothing was ever found which depended upon the presence of the sample in the coil. The optimum orientation of the crystals in the coil was never determined, but some chunks of scrap quartz from Brazil and the sapphire fragments were shorter than the coil diameter, so were tried at various orientations. The clear crystals, large size and high oxygen content of the samples used in these tests should have aided in producing a detectable NQR signal.

During the pulsed-spectrometer searches at the University of Denver, the nitrogen-14 signal from a 30 ml sample of $\text{C}_8\text{H}_{11}\text{N}$ was measured; a 60 mv signal amplitude was obtained from about 2.3×10^{23} nuclei of ^{14}N . The same sample volume of quartz was estimated to contain only 4.5×10^{20} nuclei of ^{17}O , because of its low isotopic abundance. On the other hand, according to Pen'kov and Sofin (1967), the (gyromagnetic ratio)² for ^{17}O is 3.5 that of ^{14}N (see table 2). Since the ratio: frequency/line width is unknown for ^{17}O , its influence on signal strength cannot be estimated. Consideration only of the ratios of nuclear abundance and the square of the gyromagnetic ratio led to the expectation that a quartz sample should have produced a signal amplitude of only 0.4 millivolt in the equipment at the University of Denver. Since the noise level was 1 to 2 mV, no further serious searches for the ^{17}O resonances were made.

Subsequently, conversations with Prof. P. J. Bray of Brown University, a respected senior NQR researcher, indicated that the ^{17}O resonances had never been observed except in "heavy ice," obtainable from Israel enriched with 100 times or more the 0.037% isotopic abundance of ^{17}O found in all natural materials. Still later, a reference was found (Brun, et al, 1970) to what was believed to be the first observation of the quadrupole effect in ^{17}O without artificial enrichment. The signal was enhanced by a large but unknown factor by employing the Overhauser effect (Abragam & Borghini, 1964). This apparently can be done only in a standard NMR experiment and requires in addition, a very low temperature in the liquid helium range and a strong transverse r.f. magnetic field at the resonant frequency of the electron system (9 to 72 gigahertz).

The paramagnetic chromium-ion doping in the ruby specimen used was apparently necessary to fulfill the requirement of an energy-saturated electron system.

In the experiment of Brun, et al (1970), new values of the quadrupole coefficients of ^{17}O in corundum were found: $\text{NQCC} = 2.167 \text{ MHz}$ and $\eta = 0.517$ at 1.9°K . These should be slightly different at room temperature, but would nevertheless indicate that the pure NQR lines should be found at 0.406 and 0.622 MHz, very far from the values given in table 4 on the basis of theoretical calculations by Hafner and Raymond (1968). It is not surprising that we never saw the upper one in the course of searching the frequency range between 0.5 and 1 MHz for the upper ^{27}Al resonance, in view of the delicate, complicated and artificial laboratory procedure required in the experiment of Brun, et al (1970). Neither such procedures, nor artificial oxygen-isotope enrichment of the rock samples are possible as a part of a borehole or field method of measuring rock stress.

2.6 CONCLUSIONS REGARDING THE USE OF NQR

The outlook is now rather poor for the eventual use of the NQR's of ^{27}Al , ^{23}Na and ^{39}K in feldspars to measure rock stress. The feldspar NQR signals of ^{27}Al appear to be substantially weaker than the ^{27}Al signal of pure corundum (Al_2O_3), which was itself barely detectable by a sophisticated laboratory technique. This is probably because of the lower concentration of aluminum, plus colored impurities, in the feldspars. The same consideration would apply to ^{23}Na and ^{39}K .

A major impediment to the use of all three isotopes, as well as ^{17}O , appears to be the comparatively low frequency of the resonances; most radio-frequency spectrometric methods become more sensitive at higher frequencies. One basic reason for this is that the voltage induced in a coil by nuclear or electronic magnets is proportional to the frequency of their emissions, in accordance with Faraday's law of electromagnetic induction. From a quantum point of view, the energy of interaction per particle is proportional to the frequency.

In all the advanced NQR experiments performed, samples of 50 gm or less were used. There is some possibility that the use of larger samples (e.g., 5 kilograms) would enhance the NQR signals of feldspars enough to make them detectable. However, a practical method of measuring rock stress in situ will involve a considerable further degradation of the signal, because the rock sample is not all feldspar, and it cannot be inside the coil but only adjacent to it or surrounding it. Further quantitative experiments would be needed to determine the detectability of NQR signals from large, external rock samples as found in a drill hole.

The outlook for using ^{17}O to measure rock stress is substantially worse than that for ^{27}Al or ^{23}Na , because of the much lower abundance of this isotope in natural rock-forming minerals.

3. NUCLEAR MAGNETIC RESONANCE METHODS

Conventional NMR has received by far the greatest amount of research of any of the radio-frequency spectroscopic methods. An entire research journal, Nuclear Magnetic Resonance, has been devoted largely to this subject since 1968. The nucleus receiving the bulk of the effort has been the proton, because hydrogen is a prominent constituent of water and most organic compounds, and because it gives a particularly strong NMR signal. Material in the liquid state is best for NMR, since the rapid molecular motion in liquids averages out the magnetic disturbances from neighboring atoms and permits sharp resonances of the nucleus with the external fields.

NMR occurs only in the presence of a highly uniform, steady external magnetic "aligning" field, about which the spinning magnetic nuclei can precess. The precession couples magnetically with coils surrounding the sample, whose axes are perpendicular to the aligning field, as shown in figure 10. The frequency of resonance is given by:

$$f = \mu H_0 / h I \quad (6)$$

Here H_0 = aligning field strength in gauss.
 h = Planck's constant = 6.62×10^{-27} erg sec
 I = nuclear spin number
 μ = nuclear magnetic moment

For example, in a field H_0 of 5000 gauss, typical of those generally used, hydrogen nuclei resonate at 21.3 MHz. The earth's field, however, is sufficiently uniform over a sample to be used for alignment. For a typical earth's-field strength of 0.5 gauss, the proton resonance occurs at 2,130 Hz. Excellent digital magnetometers exist which employ NMR in this way. The sample, of highly purified water, hydrocarbon, or alcohol, must have a volume greater than about 500 ml to obtain sufficient NMR signal. The protons are pre-aligned by a strong but non-uniform dc field from a pulsed coil before each measurement interval; when the pre-alignment field is removed, the protons remain sufficiently aligned in the earth's field to give a strong NMR signal for about 1 second, the spin-spin coupling relaxation time T_2 . This time is made long enough by having a very pure liquid sample.

3.1 FINDINGS OF THE NMR LITERATURE STUDY

A Swiss group has demonstrated the feasibility of NMR studies of several organic liquids in the earth's field, with or without a strong pre-aligning field (Béne, 1966). Through successive improvements in equipment, ending in that shown in figure 11 (Merck, et al, 1967), they have achieved a resolution of 0.06 Hz. They had sufficient sensitivity to detect weak satellites of the proton resonance, caused by interaction with rare isotopes such as carbon-13, which constitutes about 1% of the carbon in organic liquids. Figure 12 shows the satellite group found for methanol, CH_3OH . The calculated spectral lines are shown below as vertical bars.

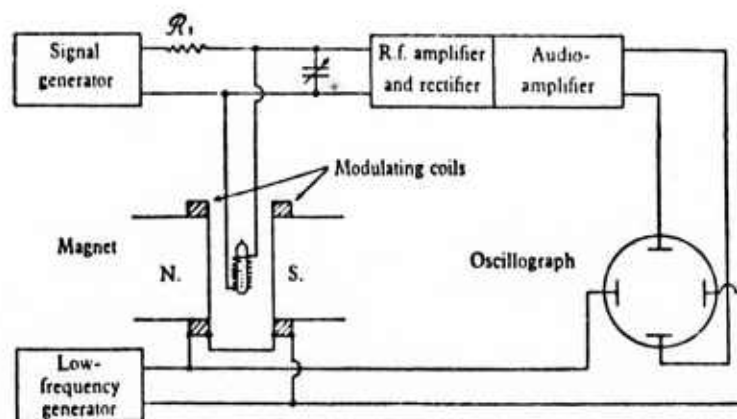


Figure 10. Schematic diagram of Rollin's arrangement for observing nuclear magnetic resonance (from Andrew, 1954)

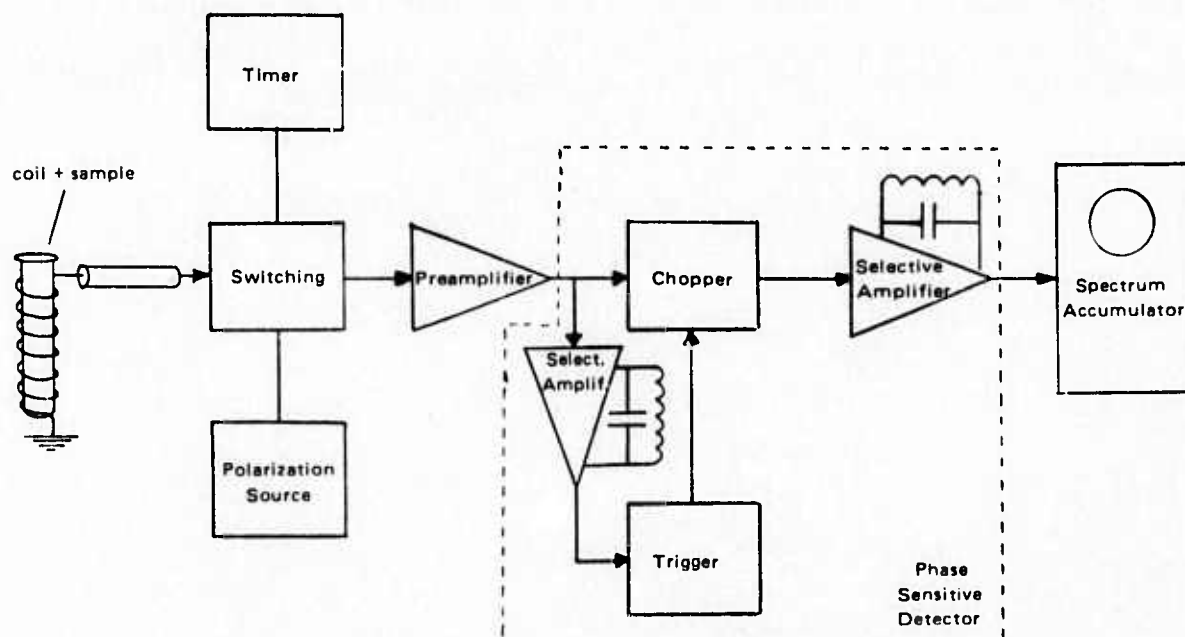


Figure 11. Equipment for NMR in the earth's magnetic field (from Merck, et al, 1966)

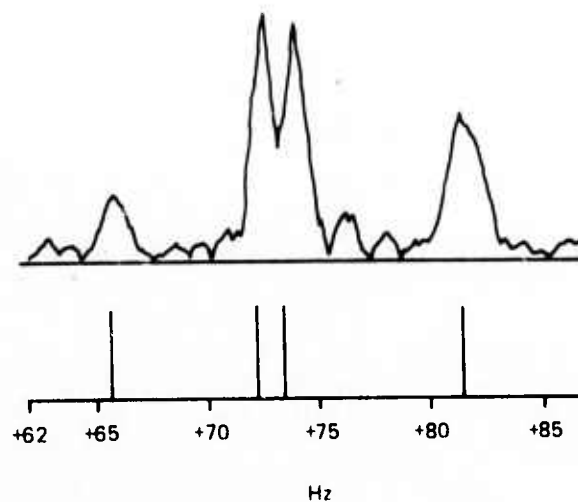


Figure 12. Proton satellite resonances for the $^{13}\text{C} - ^1\text{H}$ band in CH_3OH (from Béné, 1966)

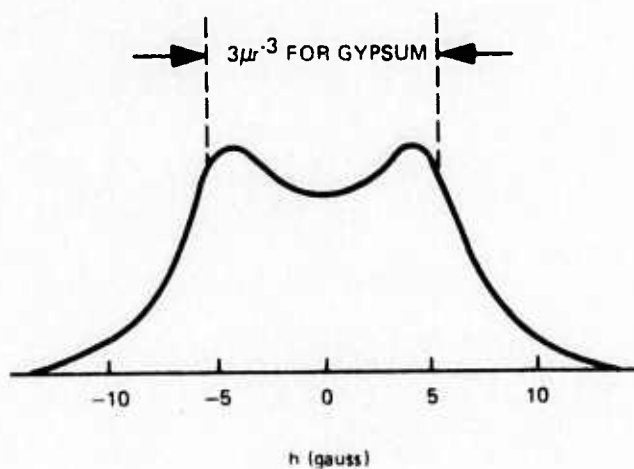


Figure 13. Resonance line shape for the protons in polycrystalline gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, taking into account the interaction of all neighbor atoms (from Andrew, 1954)

The frequencies of such satellites should be stress-sensitive, since they depend upon the separation of the protons from the ^{13}C atom in the molecule.

It appears that a similar scheme might be considered for NMR measurements of rock stress in the earth's field. Numerous solids, including the natural minerals Al_2O_3 (corundum), CaF_2 (fluorite), $\text{LiAl}(\text{SiO}_3)_2$ (spodumene), BeAl_2O_4 (chrysoberyl), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum), H_2O (ice), and glass have been investigated structurally (at high fields) by NMR (Andrew, 1969). Besides hydrogen, about 10 nuclides including ^{27}Al , ^{17}O , ^{29}Si , and ^{43}Ca have been detected in minerals by NMR. Signal strengths are low, resonance patterns are very broad and their detailed structure is badly blurred, particularly for polycrystalline samples, as shown in figure 13 for gypsum. Nevertheless, it has been shown that the mean-square width of the resonance (its "second moment") is often proportional to r^{-3} , where r is the mean separation between pairs of resonating nuclei, hence, the NMR pattern width is very sensitive to r , which has been measured to a precision of 0.4 percent via NMR pattern widths. Since r changes under mechanical stress, rock stress can be measured by NMR, in principle.

In many solids the resonance pattern width is determined largely by local magnetic fields from neighboring nuclei. For example, the gypsum curve of figure 13 consists of overlapping resonances from the two protons in the water of hydration. Each perturbs the magnetic field at the other by an amount $\mu/r^3 = \pm 5$ gauss, equivalent to a minimum pattern width of 42.3 kHz, which could only be plotted with a higher center frequency. This would require an external aligning field of perhaps 50 gauss, obtainable in the central region of a 4000 ampere-turn loop 50 cm in radius, for example. The practicability of such a scheme requires further study, since unavoidable nonuniformities in the aligning field might broaden and weaken the gypsum pattern further.

Line widths for protons in 32 minerals are tabulated by Marfunin (1965). They range from 0.1 gauss (425 Hz) in kaolinite to 11 gauss (4.7 kHz) in bauxite. Most would require a strong artificial aligning field to be observed.

In part, the line width in solids appears to depend in a complicated way upon the spin-spin and spin-lattice relaxation time T_2 and T_1 , which in turn depend on composition, particularly on traces of paramagnetic impurities (Bloembergen, 1961). Generally T_2 is short and T_1 long compared to the values for liquids, which results in a poor signal-to-noise ratio. Andrew (1969) states that the NMR spectrum of a solid can rarely be presented on an oscillograph, and instead its first derivative is usually recorded using a phase sensitive amplifier.

An encouraging precedent for earth's field NMR in solids exists in that the ^7Li and ^{19}F resonances in a very pure sample of LiF (with a very long relaxation time) have been measured in the earth's field by use of a strong pre-aligning field (Ramsey & Pound, 1951). Although the pattern was about 200 kHz broad, there were peaks at the central resonant frequencies of these elements.

3.2 POSSIBILITIES FOR NMR AS A METHOD OF MEASURING ROCK STRESS

The general requirements for successful NMR of natural polycrystalline minerals in situ would appear to be as follows:

1. Pre-alignment by a strong, temporary dc field;
2. Large sample volume (several kilograms);
3. Narrow resonance pattern width, of the order of 100 Hz.
4. Low r.f. power level to avoid sample saturation.

In the laboratory, requirement (3) is met in many materials by working at very low temperatures. In our application this is not possible; our best alternative is to select an "indicator" mineral with inherently sharp resonances.

We concluded that rock-stress measurement by NMR may be difficult to develop and experiments would not be attempted until the possibilities of NQR had been explored. Nevertheless, NMR offers the possibility of employing several additional minerals as stress transducers, since there are many elements capable of NMR but not NQR, such as hydrogen and silicon, which are prominent in natural rocks. The possibility of using NMR should be left open, for the present.

3.3 ZERO-FIELD NMR OF MAGNETICALLY ORDERED MINERALS (ZNR)

In magnetically-ordered (ferromagnetic, ferrimagnetic, or antiferromagnetic) crystals, there is a strong internal magnetic field arising from the electron spins and orbital currents coordinated by strong coupling between nearby atoms. In this field any nucleus present which has a magnetic moment will have a built-in resonance frequency.

Several magnetically-ordered minerals occur as accessory minerals in common rocks. As noted on page 8 of this report, igneous rocks contain an average of 1 to 2% of ilmenite, $\text{FeO} \cdot \text{TiO}_2$, which has a magnetic susceptibility of 0.03 to 0.14 cgs units (Jakosky, 1950). Magnetite, Fe_3O_4 , has a susceptibility of 0.04 to 24 cgs units (Jakosky, 1950) and occurs as very fine particles in basalt and other dark igneous rocks. It provides the basis, together with its mixtures with ilmenite and ulvospinel (spinel = $\text{MgO} \cdot \text{Al}_2\text{O}_3$), of the science of paleomagnetism (Dunlop, 1973). Magnetite also constitutes from 20 ppm to 0.2% of most terrestrial soils (Cook and Carts, 1962), so presumably occurs also in sedimentary rocks such as shales and dark sandstones, since it is a chemically resistant mineral. Other "magnetic" minerals found widely distributed in nature include maghemite, (γ - Fe_2O_3) suspected in basalts (Dunlop, 1973) and in red soils and rocks (Cook and Carts, 1962), and some of the garnets (common black garnet = $3 \text{ CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$).

The joint effect of these minerals in producing magnetic susceptibility (Jakosky, 1950) permits the estimation of the equivalent percentage of magnetite (assumed susceptibility = 0.2 cgsu from Dunlop, 1973) in typical major rock types, as summarized below:

Table 6. Estimated magnetite content of rocks

<u>Rock</u>	<u>Rock susceptibility, cgsu</u>	<u>% "magnetite"</u>
Basalt	0.00068 to 0.0063	0.3 to 3
Granite	0.00003 to 0.0027	0.015 to 1.3
Gneiss	0.00001 to 0.002	0.005 to 1.
Schist	0.000026 to 0.00024	0.013 to 0.12
Shale	0.00004 to 0.00005	0.02 to 0.025
Sandstone	0.000005 to 0.000017	0.0025 to 0.008
Limestone	0.000004 -	0.002 -

It is apparent that the ZNR of magnetite and related ferrimagnetic minerals could furnish a basis for a widely applicable stress-measuring method for rocks, providing the effect is strong enough and has a suitable pressure coefficient. The 45.5 MHz resonance of iron particles measured by Kowallis in zero applied magnetic field was a ZNR (Benedek, 1965). That particular resonance is of only passing interest here, since free iron is almost never found in the earth. We have confined the small amount of effort on ZNR in this program to magnetite.

No attempt was made to survey the extensive published literature on the NMR of magnetic materials (ZNR). Most of it deals with synthetic ferrites and garnets, and miscellaneous inorganic compounds rare or absent in nature. Andrew (1972) lists 29 recent references to this work. The active nuclei used as "probes" within the various compounds included hydrogen, vanadium, manganese, fluorine, iron-57, europium, etc. Very little of this work is of any interest to this program.

From a reference (Portis and Lindquist, 1965) given us by Dr. Moulton at the Florida State University, it was learned that zero-field resonances had been found in magnetite at 67.621 and 63.549 MHz, and haematite, α - Fe_2O_3 , resonates at 71.5 MHz at room temperature. The signal-to-noise ratio of the upper magnetite resonance was reported to be "very good" and the line "sharp" (Ogawa and Morimoto, 1962); the temperature coefficient of the resonances of both magnetite and natural haematite was found to be $3.6 \times 10^{-4}/\text{deg C}$, with frequency decreasing as temperature is raised. Through inquiries, we learned of recent precise work on magnetite at the Naval Research Laboratory and obtained a preprint of a new paper giving the resonance line shapes (Rubinstein, Stauss and Bruni, 1973). These are reproduced for room temperature in figure 14. At liquid helium temperatures, the upper line narrows and can be resolved into four components, each only about 0.3 MHz wide (that is, 0.4% of the frequency). The room-temperature line is about 1.2 MHz wide, but the position of its peak might be measured to within 0.25 MHz or 0.35% of the frequency. However, George Stauss of NRL explained that the line shapes

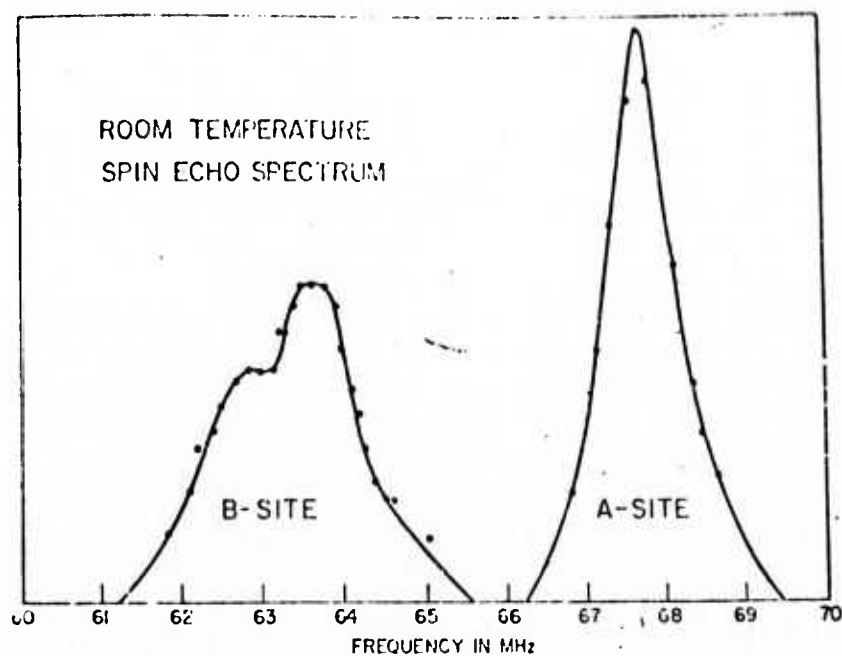


Figure 14. Room-temperature, zero-field, pulse-echo NMR spectrum of ^{57}Fe in magnetite (from Rubinstein, Stauss and Bruni, 1973)

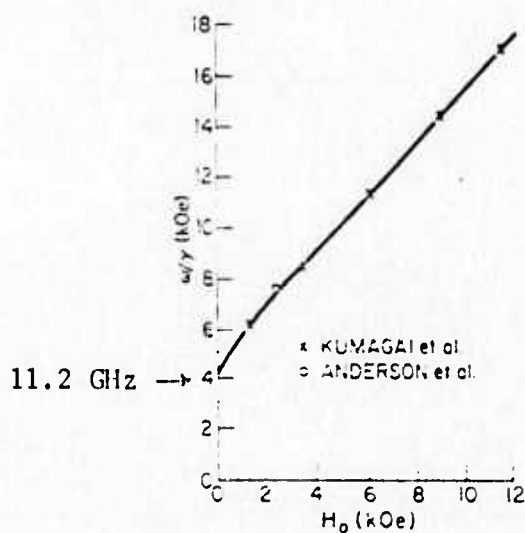


Figure 15. Antiferromagnetic resonance frequency versus applied field H_0 for $\alpha\text{Fe}_2\text{O}_3$, (from Foner, 1963)

shown in figure 14 were smeared by the pulse width of 5 microseconds used, and that a c.w. spectrogram should give better resolution.

3.3.1 Experiments

The marginal-oscillator c.w. spectrometer at Teledyne Geotech was again modified to operate at frequencies from 47.5 to 72 MHz, and samples of powdered magnetite and ilmenite, diluted with 50% or more of sugar or salt (to insure good penetration of the r.f. magnetic field) were empirically tested for resonances. Nothing was found but spurious equipment resonances which could not be eradicated. Oscillations were very weak, so the frequency counter and oscilloscope were unreliable. Since these tests were made near the end of the program period, no attempt was made to build a new spectrometer more suitable for this frequency range, and to insure that the r.f. field was below the rather low saturation threshold for magnetite.

3.3.2 Further Consultations

In conversations with several research people familiar with ZNR in magnetite, it developed that they considered these resonances weak and difficult to detect; the chief reason is that ^{57}Fe comprises only 2.45% of the iron present. No published measurement of the pressure coefficient was known. George Stauss attempted, at our request, to assemble equipment to measure it, but was unable to do so in the short time available, especially since magnetite work was being terminated at NRL. However, it was learned that the pressure coefficients of other "hyperfine resonances" amount to 0.01 to 0.1% of the frequency per kilobar. (The pressure coefficient for haematite may have been published by David Anderson in the Physical Review about 1966, but was not looked up.) Finally, preliminary data were obtained on the pressure effect on three internal magnetic fields of magnetite at room temperature, as obtained by Dr. Nicholas Halasa at the University of Illinois by Mossbauer Methods (private communication). These field changes, which imply a decrease in the upper (tetrahedral) resonance frequency with increasing pressure, average approximately 2.2% for 100 kilobars (1,400,000 psi). This is a disappointingly small effect, and is within the range stated above for hyperfine resonances.

3.3.3 Conclusions on ZNR

If it can be assumed that under ideal conditions, the frequency of the upper magnetite resonance can be measured to a precision of 0.08 MHz or 0.12%, this would mean a pressure resolution of 5.5 kilobars or 76,000 psi. This would not be useful for practical rock stress measurements. It would be necessary to postulate measurements to a precision of 1 kilohertz or better to resolve 1,000 psi, which would be an excessive and indefensible extrapolation of present technology. In view of the very low concentrations of magnetite in most rocks (table 6), the low content of ^{57}Fe in magnetite, and the reported weakness of the resonance signals, it appears that the ZNR method has very little chance of success as a means of measuring rock stress.

4. ELECTRON PARAMAGNETIC RESONANCE (EPR)

This type of resonance (Bleaney & Stevens, 1953) has been observed in ions of three groups of crystalline salts (among other substances), as follows:

1. Alums, fluosilicates and Tutton salts of the "iron group" isotopes shown in table 7.
2. Rare earth salts of elements from atomic number 57 (lanthanum) to number 71 (lutecium). These are in actuality not particularly rare elements.
3. Actinides, including uranyl, neptunyl and plutonyl salts.

Table 7. The Iron Group Isotopes with I \neq 0

<u>Symbol</u>	<u>Atomic number</u>	<u>Name</u>	<u>Mass number</u>	<u>Natural abundance</u>
Ti	22	Titanium	47	7.5%
Ti	22	"	49	5.5%
V	23	Vanadium	50	0.24%
V	23	"	51	99.8%
Cr	24	Chromium	53	9.4%
Mn	25	Manganese	55	100%
Fe	26	Iron	57	2.2%
Co	27	Cobalt	59	100%
Ni	28	Nickel	61	1%
Cu	29	Copper	63	69.7%
Cu	29	"	65	31.1%

EPR is possible with very small samples, of the order of 1 milligram, because the magnetic moments of ions are about 1000 times as strong as those of nuclei. Hence, there appears to be a possibility that the larger samples (several kilograms) within reach of the magnetic field of a resonance logging tool could be effective even where the sensitive isotope is only a trace element measured in parts per million. In fact, it is desirable that this be the case, since resonance line widths must be as narrow as possible for detection. Murfunin (1965) states that concentrations must lie between about 1 ppm and 0.5 percent. Narrow resonances can occur only when each paramagnetic ion is surrounded by several layers of diamagnetic atoms, as for example the chromium ion Cr^{+3} occurring as an impurity in corundum, Al_2O_3 , to form ruby. The iron group elements Ti, Mn and Fe are among the more abundant constituents of accessory minerals in igneous rocks. Hence, there are several natural minerals capable of EPR response.

Marfunin's excellent paper (Marfunin, 1965) summarized all known work on EPR (ESR) effects in natural minerals up to that time, including Russian measurements on over 200 mineral species from numerous localities. An enormous

literature also exists on ESR of numerous atomic species dispersed in synthetic corundum, fluorite, periclase, and scheelite, as a result of maser and laser studies (Marfunin and Bershov, 1964). Marfunin found that at room temperature, the great majority of his 200 natural specimens showed the ESR spectra of Mn^{+2} , Fe^{+3} and Cr^{+3} . He gives tables of spin-Hamiltonian coefficients determined by ESR for several common rock-forming minerals, including calcite, dolomite, apatite, corundum, rutile, spinel, fluorite, and beryl. He also observed widespread distribution of Fe^{+3} in several feldspars and in certain rare types of quartz. These data would require further study for practical application to our problem.

EPR, like NMR, requires a steady and highly uniform magnetic aligning field, since the resonant frequency f is proportional to the aligning field H , as follows:

$$f = g\beta H/2\pi h \quad (7)$$

Here h = Planck's constant = 6.62×10^{-27} erg sec
 β = Bohr magneton = 0.928×10^{-20} erg/gauss
 g = spectroscopic splitting factor = 1 to 2 +.

EPR has customarily been performed in magnetic fields of several thousand gauss, corresponding to microwave frequencies, for several practical reasons. In our application, however, the only reasonably uniform magnetic aligning field available is that of the earth, which is of the order of only 0.5 gauss. This corresponds to resonant frequencies of 0.7 Megahertz (MHz) to perhaps 1.5 Mhz, which would be suitable for practical stress logging.

The EPR line width is determined chiefly by the ion dilution and by the spin-lattice relaxation time, which is a function of the mineral and the temperature. For this reason much EPR work is done at very low temperature, which is not possible in our application. However, through a fortunate choice of mineral, it is conceivable that spin-lattice relaxation times as long as 10^{-5} second at room temperature could be found. (Times as long as 10^{-4} second have been achieved at very low temperatures.) This would produce a line width of 0.1 Mhz, which is compatible with EPR frequencies in the earth's field. At about this and longer times, saturation effects begin to degrade the line strength. The mineral chosen must also contain the EPR ion in sufficient dilution that the spin-spin relaxation time is also comparable to or longer than 10^{-5} second.

Unfortunately, EPR in many substances is anisotropic; the g -factor varies with the angles between the crystal axes, the r.f. field and the aligning field H . This means that in a polycrystalline rock where all possible crystal orientations occur, and where the direction of the r.f. field varies around the sampling coil or logging tool, the resonance will be smeared out and its amplitude reduced for magnetically anisotropic, paramagnetic substances. This further restricts the choice of the indicator mineral.

The observability of EPR effects in minerals in situ will also require adequate resonance amplitudes. These are lower at low frequencies (Bleaney & Stevens, 1953). Hopefully, this effect can be compensated for by large sample size.

We did not plan to make extensive efforts in this program to apply the EPR phenomenon to measuring rock stress. The outlook was not considered favorable for the following reasons:

1. The earth's field has apparently never been successfully tried to date as an aligning field for EPR.

2. The choice of a widely useful indicator mineral is circumscribed by constraints on mineral composition and on concentration and lattice coupling of the EPR-sensitive species that are still largely unknown.

Nevertheless, because of the fact that trace elements have produced EPR signals in numerous natural minerals, the possibility of EPR rock stress measurement was considered open. Near the conclusion of the program, as it began to appear that strong NQR signals could not be obtained from common minerals, further study of EPR was performed.

4.1 ELECTRON FERROMAGNETIC RESONANCE

One variety of EPR which initially was considered of interest is EFR or "ferromagnetic resonance" (Toner, 1963). Antiferromagnetic or ferromagnetic resonance has been observed in ilmenite in the 2 mm-4 mm wavelength range, in ruby, in haematite (microwave and infrared regions), in synthetic yttrium-iron garnet, in many oxides and fluorides of manganese, nickel, chromium and cobalt, and in a variety of alloys (Praddaude, 1972). In general, it appears that the resonance frequencies are too high for our application, even with zero applied magnetic field (figure 15). The reason apparently is the strong interaction between the unpaired-electron spin and the strong, internal magnetic fields of the crystal as a whole. It is tentatively considered reasonable not to evaluate further, the entire class of minerals exhibiting EFR.

4.2 EXPERIMENTS ON PARAMAGNETIC MINERALS

Nearly the entire bulk of EPR literature titles found in a brief search of the physics and chemistry abstract journals were concerned with synthetic and organic substances not occurring in nature. Rather than perform another exhaustive literature search under such unpromising conditions, our final policy of making maximum use of consultants and existing, commercially-developed equipment was followed once again.

A Varian model 4502-13 microwave EPR spectrometer equipped with a graphic chart recorder, a large magnet and stabilized, adjustable-sweep magnet current supply had been located at North Texas State University near Dallas. This instrument operated at a frequency of 9000 MHz and was equipped with a temperature-controlled sample cell capable of operation over a wide temperature range. Arrangements were made for Dr. Paul Jones of NTSU to test numerous samples of selected natural minerals containing impurities or color, in this equipment. Tables 8 and 9 summarize the many strong, clear resonances recorded in the initial tests. Examples of the recordings are given in figures 16 to 18. With all samples, the magnetic field was swept from about 500 gauss to 9500

Table 8. EPR "electron" resonance at 9000 MHz, 3300 gauss

<u>Sample No.</u>	<u>Mineral</u>	<u>Estimated voltage S/N for 5 gm sample and $\Delta f = 10$ Hz</u>	<u>Remarks</u>
21	Ottowa sand	38(?)	Others also, near 2500 G
15	Milky quartz	30	
5	Smoky quartz	7	
I	Orthoclase feldspar (Fremont, Calif.)	60(?)	Extrapolated
9	Orthoclase feldspar (Goodsprings, Nev.)	22	3 other large reso- nances at 1900-2700 G
7	Microcline feldspar (Pringle, S. Dak.)	13	
J	Albite feldspar (Gunnison, Colo.)	5.5	
10	Hornblende	8.5(?)	Another near 2500 G?
S	Red shale	100 (?)	Sample conductive; 0.05 gm used

Table 9. EPR "manganese" resonances at 9000 MHz

<u>Sample No.</u>	<u>Mineral</u>	<u>Estimated voltage S/N for 5 gm sample and $\Delta f = 10$ Hz</u>	<u>Remarks</u>
R	Oil shale (Colorado)	500	7 strong lines be- tween 3100 & 3600 G
14	Blue calcite	188(?)	6 strong lines be- tween 2700 & 3000 G (misread?)
9	Brown calcite	40,000(?)	6 strong lines be- tween 3000 & 3600 G

NOTE: Symbol (?) indicates a large extrapolation based on
sensitivity dial settings.

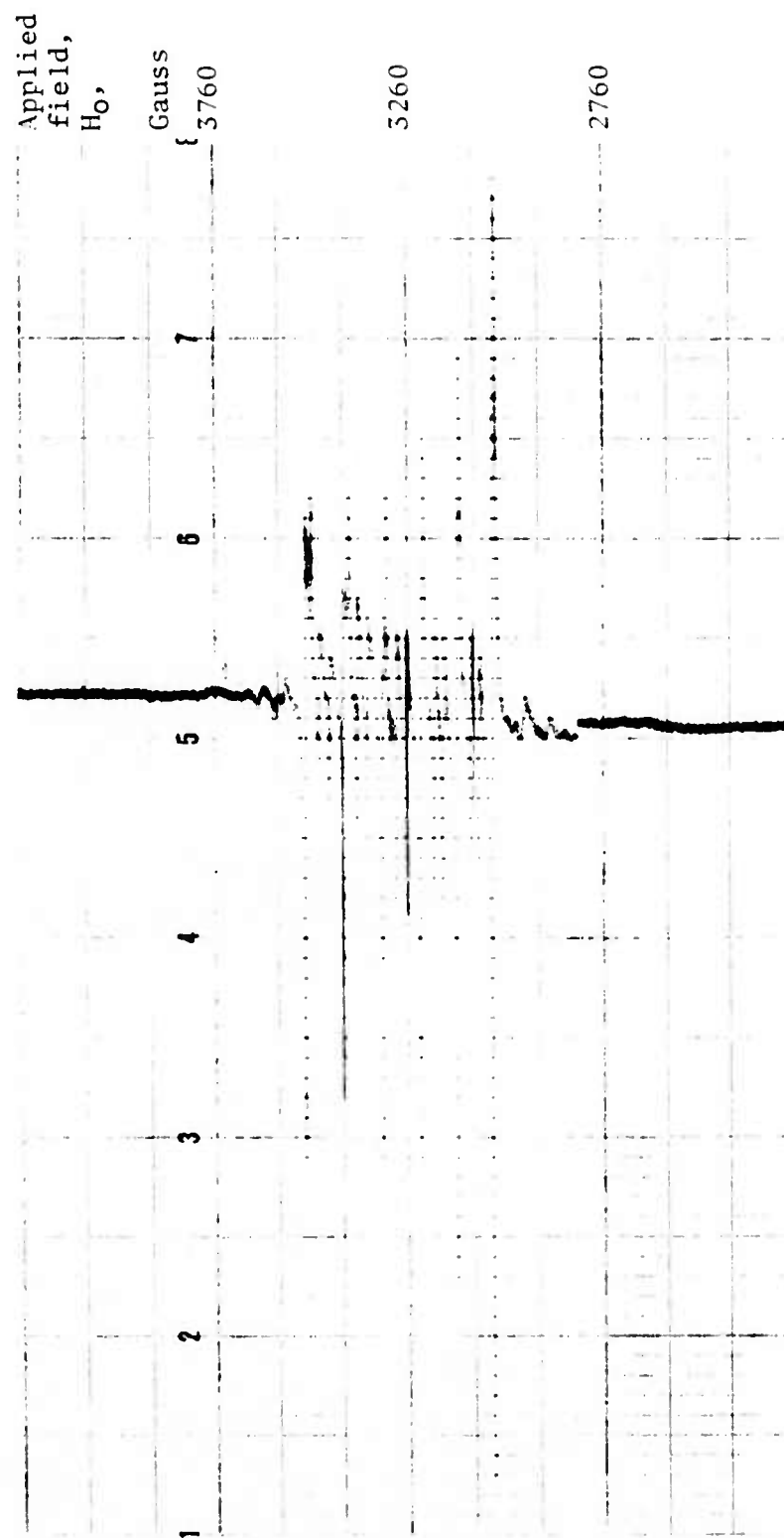


Figure 16. EPR signals from brown calcite, gain = 100, $\tau = 0.005$ sec

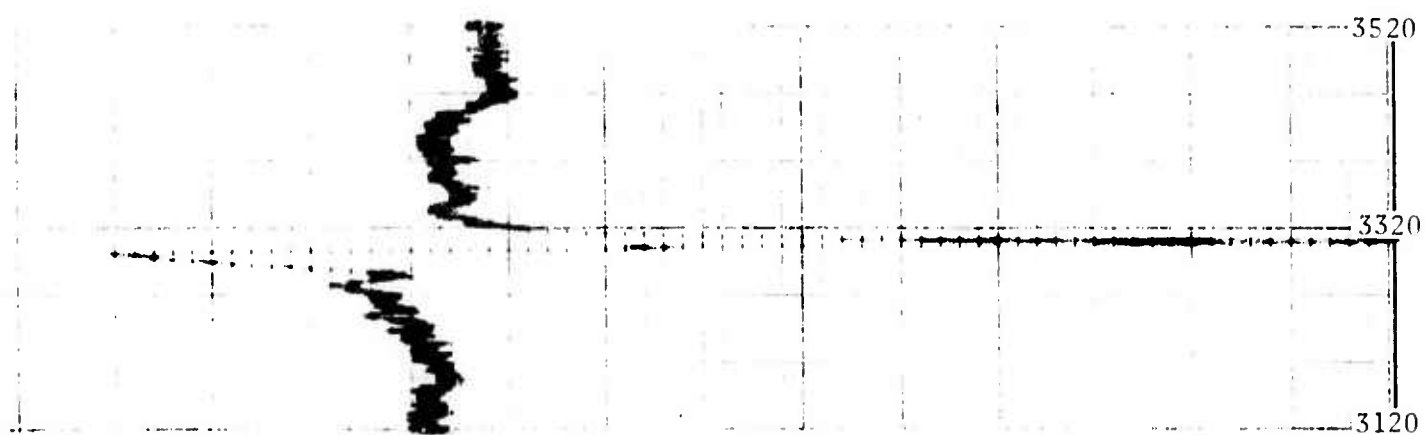


Figure 17. EPR signal from white quartz. Gain = 500,000, $\tau = 0.1$ sec

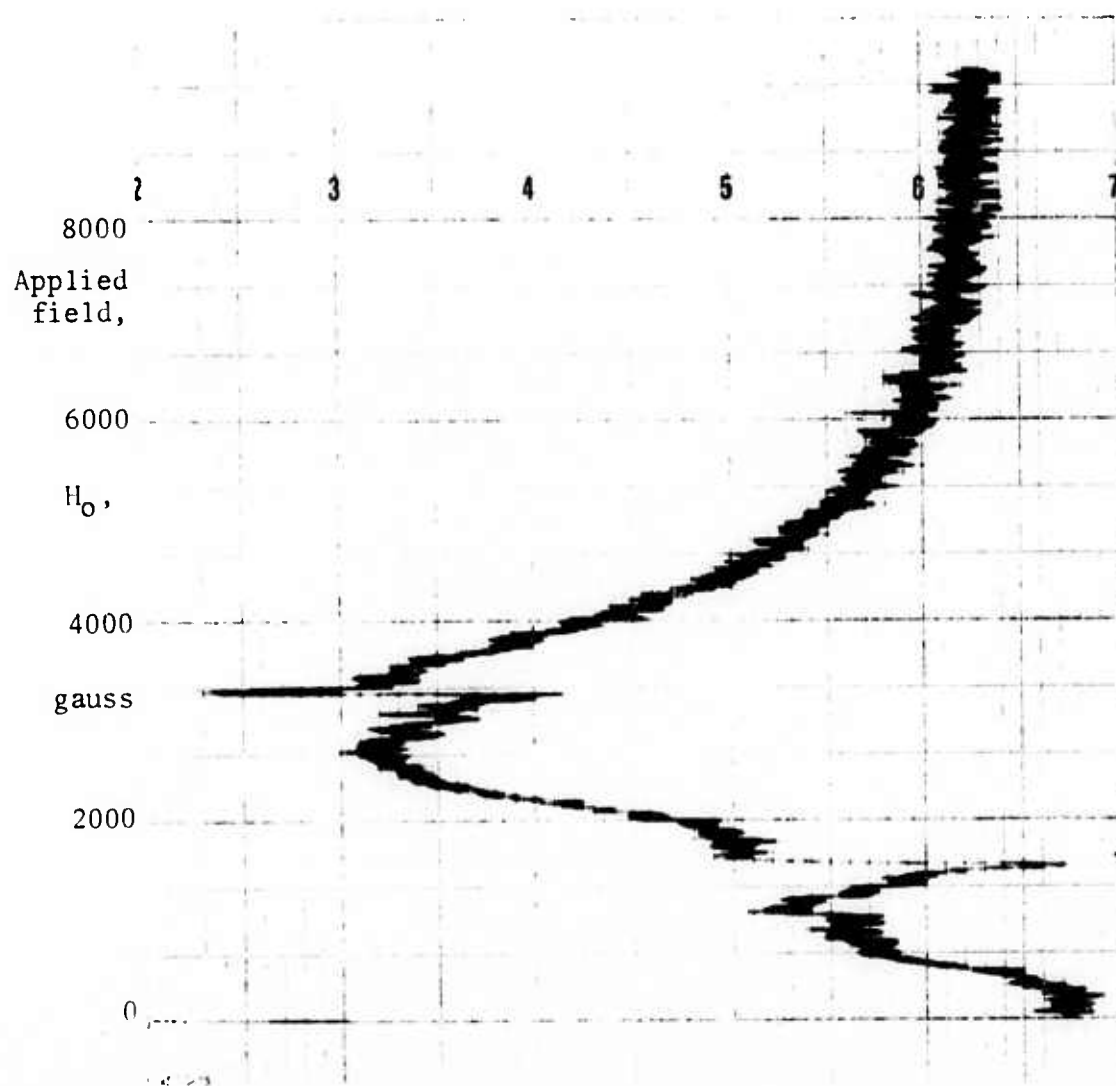


Figure 18. EPR signal from S. Dakota microcline. Gain = 125,000, $\tau = 0.1$ sec

gauss over a 5-minute interval. Any resonances seen were re-recorded with a narrower magnetic range and better choices of gain, filter τ and sweep time, to obtain good resolution of the resonance width or slope.

The group of 6 lines centered at 3,300 gauss in the brown calcite (figure 16) can probably be identified by their number and field value as due to manganese (Mn^{+2}) ion impurity, according to Dr. Jones (personal communication); the six transition energies are produced by splitting of the electron absorption line by coupling to its nucleus of spin $I = 5/2$, which has six possible states. This identification agrees with that of Weeks (1973) for a six-line EPR group found in a feldspar. The single resonance found near 3,300 gauss (Landé splitting factor $g \approx 2$) in most of the minerals can be attributed to single, loosely-coupled electrons which produce color in many compounds. Figures 17 and 18 show this resonance well, and it no doubt accounts for the central line in the group of 7 in oil shale (table 9).

In records made at high gain, a line near 1525 gauss, some 50 gauss wide always occurred. This was found also with an empty sample tube, and is attributed to a slight contamination by iron (Fe^{+3}) in the pyrex glass of the tube. A number of other signals, including broad ones such as that seen in figure 18, have not yet been explained.

Preparations were immediately made to obtain temperature and pressure coefficients of some of the observed resonances. Pressure test cells were made up from 7 mm o.d. paper-phenolic, epoxy-fiberglass and pyrex glass thick-walled tubing, capable of being placed in the chuck of the x-band sample cavity of the EPR spectrometer. Each was anchored in a 1/2-inch pipe bushing by threads or a flange (on the glass) and sealed with epoxy cement or a neoprene O-ring. A compact pressure source consisting of a pair of high-pressure needle valves was connected to the cell and to a 5000 psi gauge, with the entire system filled with a liquid of good wetting and electrical insulating properties (trichloroethylene). When the valve stems were screwed in, their displacement readily developed several thousand psi of hydrostatic pressure in the liquid. The phenolic tube was tested to 4,700 psi before a pinhole leak developed, but it proved to have too much electrical absorption for use in the x-band EPR spectrometer. The epoxy-fiberglass tube leaked at 2,200 psi. The pyrex tubes could withstand 5000 psi momentarily, and 1000 psi for at least 30 minutes, but all split at 2000 to 3000 psi after about 5 minutes. All pressure tests were therefore run at 1000 psi, with occasional extra tests at 2000 psi. To prevent contamination of the microwave cavity, a thin gum-rubber boot was always fitted snugly over the sample tube. This boot did not appear to produce any extra EPR signals. About 12 pyrex sample tubes burst within this boot without mishap. After initial tests showed that the valves and gauge were subject to dangerous magnetic forces when attached directly to the sample tube fitting, a 2-ft length of fine stainless-steel capillary tubing was used for interconnection. Porous plugs of paper were necessary to keep all fittings completely filled with liquid while the joints were made up; even a small air bubble would prevent the pressure from developing. Figure 19 shows the final pressure-testing system used.

Table 10 summarizes the minerals tested in the pressure and temperature cells. In the latter, the sample was alternately cooled to 30°C and electrically heated to 200°C by a stream of nitrogen gas. A careful comparison of the

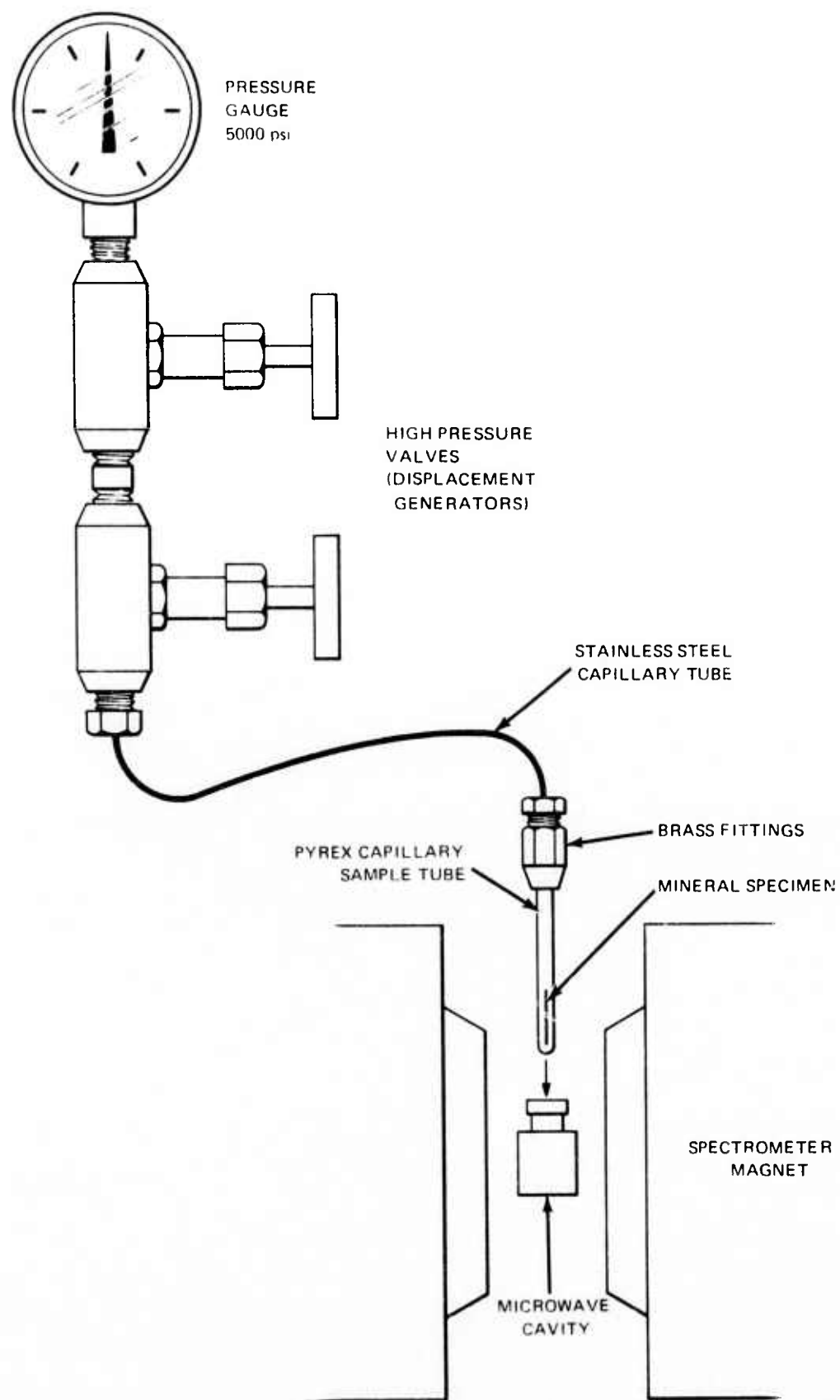


Figure 19. Arrangement for pressure-testing of EPR frequencies

spectra failed to show any temperature shifts of frequency greater than 0.1% of the frequency (or field strength), which was the limit of resolution. However, weakening and broadening of some lines did occur at the higher temperature. It is apparent that the frequency coefficients of temperature for all these minerals is less than $6 \times 10^{-6}/\text{deg C}$, which is encouraging.

Despite careful comparison of record pairs on a light table, no frequency shifts with 1000 psi of hydrostatic pressure could be seen that were greater than the resolution limit of 0.3%, except for a -0.6% shift in biotite and a +0.4% shift in blue salt (which had received 10^6 rads of gamma radiation in the AEC's Project Salt Vault). If verified, these shifts are very substantial, of the order of 3% per kilobar, which would permit usable resolution and precision in the measurement of rock stress. We were unable to repeat and confirm these measurements for lack of time and funds under this program. It would be desirable to re-run all the EPR pressure tests with special microwave fittings to which much greater pressures could be applied.

Table 10. Minerals tested for EPR shifts with
temperature and pressure

<u>Mineral</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Effects seen</u>
Brown calcite	X	X	None
Milky quartz	X	X	None
Orthoclase	X	X	None
Hornblende	X	XX	None
Biotite	-	X	-0.3% shift
Bituminous coal	-	X	None
Blue salt (NaCl) (10^6 rads γ -rays)	-	X	+0.4% shift

Figure 20 shows the sharp resonance at 3296 gauss, with two weak satellites from electron interaction, obtained from a 1-gm sample of coal. The spacing of these satellites should be pressure-sensitive, but they could not be seen during the pressure experiment because only a 1 mgm sample could be kept submerged in the trichlorethylene in the 1 mm bore of the pyrex sample tube. Figure 21 shows the complicated spectrum obtained from blue salt; those with and without 1000 psi of pressure were nearly identical. The spectra of biotite and hornblende were qualitatively similar to figure 18.

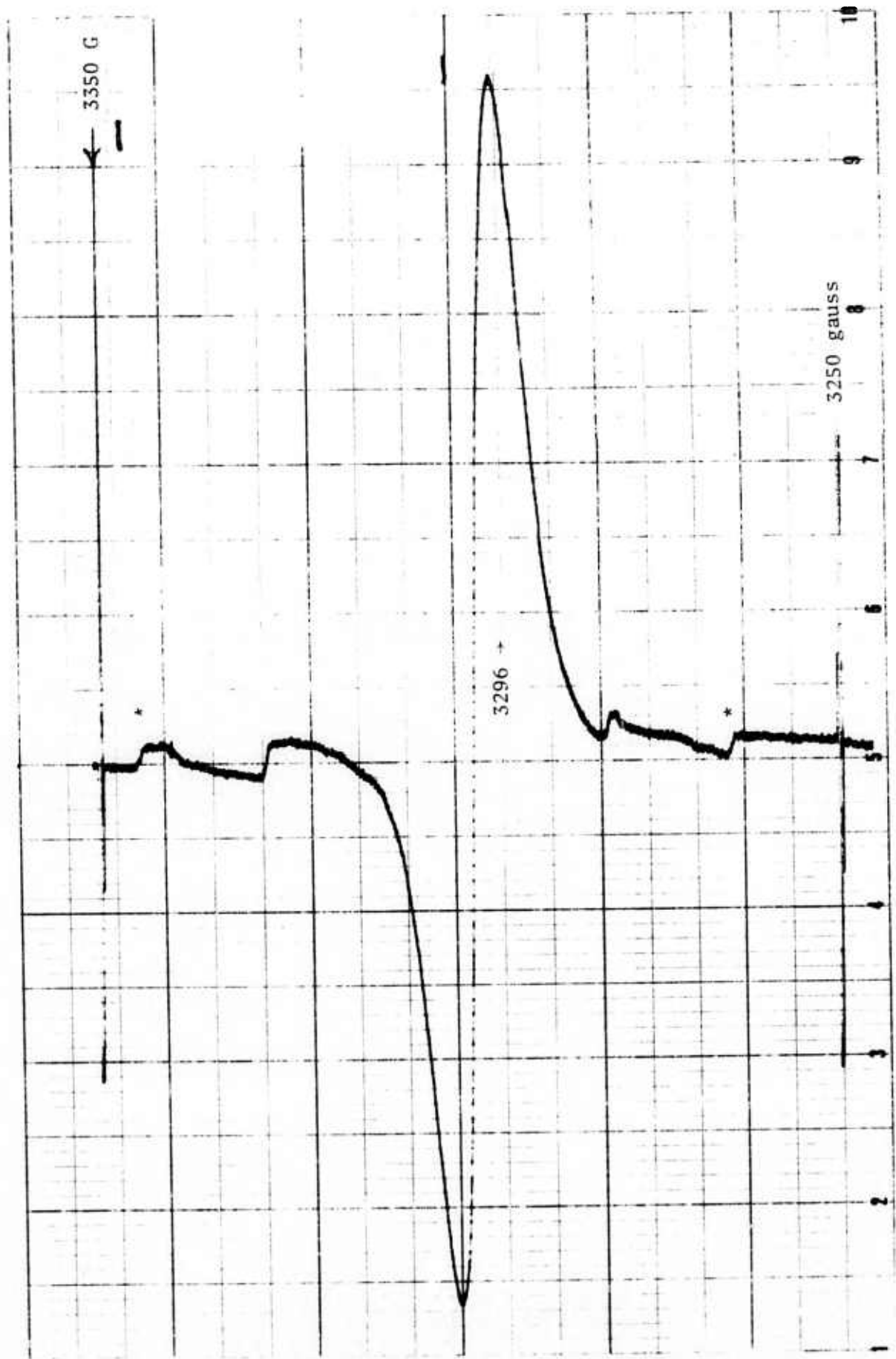


Figure 20. Magnified coal EPR signal, showing satellites (*). Gain = 400, $\tau = 0.003$ sec

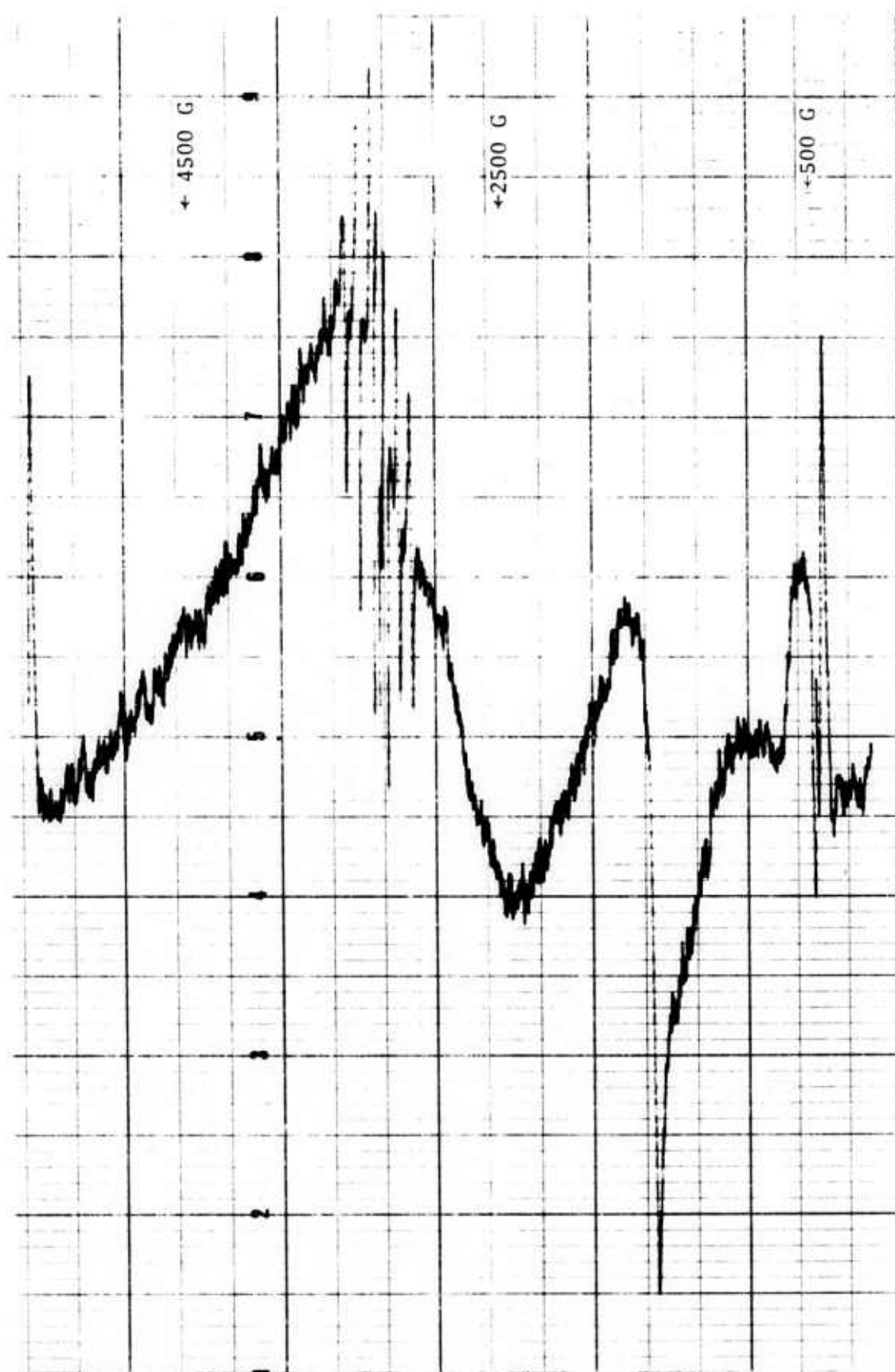


Figure 21. EPR spectrum of gamma-irradiated (blue) salt. Gain = 500,000 $\tau = 0.3$ sec

4.3 DISCUSSION ON EPR FOR ROCK STRESS MEASUREMENT

It is clear that strong EPR signals can be obtained from many minerals with laboratory-type microwave equipment. There are indications of pressure shifts of the resonances, and theoretical grounds for expecting pressure effects, at least in lines arising from coupling between different particles. Investigation of these matters in the literature and by experiment could only be begun under the present program.

A substantial question remains, with regard to the electronic measurement of rock stress, whether EPR lines can be obtained and the effect of pressure upon them can be measured at frequencies of a few MHz, using only the earth's magnetic field for alignment; alternatively, whether a synthetic magnetic field can be produced around a borehole by properly spaced solenoids, or in the wall of a mine by a large loop, that will be homogeneous enough to form EPR lines at a somewhat higher and more favorable frequency. One or the other will be necessary to adapt EPR to rock stress measurement.

Some guidance has been obtained from the literature and from consultants. Bleaney and Stevens (1953) mention that many EPR line widths are of the order of 6 gauss, or 30 to 300 MHz, so that a somewhat higher frequency is required for resolution. Line separations are also substantial (see figure 16) and it may be necessary to present two lines on the same scan. Furthermore, signal amplitude increases with frequency (Orton, 1968), partially compensated for by the accompanying change in sample size (McMillan, 1968). On the other hand, microwaves cannot be used with metallic or otherwise lossy samples, and UHF or VHF fields must be used. Decors and Fric (1972) give a design for a sensitive EPR spectrometer operating at 40 to 210 MHz, and many references on the subject. Such a spectrometer would require a d.c. magnetic field H_0 of only 16 gauss or so!

Inquiries, particularly to Sam Weiman (of the University of Wisconsin ?) brought forth a number of encouraging facts: The Varian Company once produced a 60 MHz spectrometer employing a 25 gauss magnet (see Journal of Chemical Physics, about 1963 - author: Acrivos). The splitting of the proton line still occurs at zero field in some materials, and gives a "sharp" resonance at 54 MHz, and a signal-to-noise ratio of 3 to 10 for a 2 ml sample. Dr. Dan Kivelson at UCLA did a study of relaxation processes vs pressure. The Philips Company published a study of manganese in zinc sulfide at UHF frequencies before 1966. James Burgess' thesis, published in the Physical Review on organic EPR work, employed a 1000 MHz, 300 gauss spectrometer using a 30 cm cavity and a 1-inch by 10-inch sample, which could be lossy. We have not been able to follow up these promising leads under the present program.

5. RECOMMENDATIONS

On the basis of this preliminary study, the Principal Investigator recommends further R and D on the possible application of the electron paramagnetic resonances (EPR's) found in most impure minerals, to the measurement of rock stress.

Two other methods, NMR of hydrates and other selected minerals in the earth's field, and NQR with very large samples of rock containing feldspars, also appear to merit some additional study.

Further investigations of NMR in ferromagnetic accessory minerals such as magnetite (ZNR) and of electron ferromagnetic resonances (EFR) are not recommended.

APPENDIX 1 to TR 73-7

PROPAGATION OF RF FIELDS THROUGH ROCK

PROPAGATION OF RF FIELDS THROUGH ROCK

Many rocks are surprisingly "transparent" to electromagnetic radiation in the radio-frequency range. This is particularly true of the hard rocks, which are of special concern in deep mining and tunneling projects where the measurement of rock stress is important. This is because the harder rocks (excepting some porous quartzites) are usually massive and crystalline and contain relatively little uncombined water. The moisture content, in turn, largely governs the electrical conductivity σ , which in turn determines the rate of absorption of a propagating electromagnetic wave. Wave absorption may be taken as a measure of the propagation loss for a non-radiative (Coulomb) r.f. magnetic field from an exploring coil.

The attenuation factor α determines the magnitude vs distance x , of a magnetic field H in a propagating plane wave in accordance with the formulas:

$$H = H_0 e^{-\alpha x}, \quad \alpha \doteq \left(\frac{\sigma}{2}\right) \sqrt{\mu/\epsilon} \doteq 120\pi(\sigma/2)\sqrt{\kappa}$$

in m^{-1} where σ is in mhos/meter, κ is the relative dielectric constant and μ the magnetic permeability is assumed to be close to that of free space.

There is an r.f. conductivity σ equivalent to all r.f. losses regardless of mechanism, which can readily be measured on an r.f. bridge. A fresh rock specimen is cut to fit as the dielectric in a small parallel-plate condenser; the capacitance and loss tangent are measured with and without the rock dielectric, and from the results $\sigma (=1/\rho)$ and κ can be obtained by appropriate formulas. The process is fully explained elsewhere.* From these results α , and therefore a typical propagation distance $D=6.9/\alpha$ for 60 dB of attenuation can be calculated.

Tables A, B, C, and D list parameters recently measured on four types of rock encountered in current tunneling projects:

A - Massive limestone from the Gran Sasso vehicular tunnel project near L'Aquila, Italy.

B - Granites from the St. Gothard vehicular tunnel project in the Swiss Alps.

C - Schist from the Washington, D.C., subway project.

D - Red shale from the Irondequoit sewer tunnel project near Rochester, N.Y.

The data taken at 1 MHz are of greatest interest for this program. Propagation distances d for 6 dB of field attenuation, a reasonable figure for stress measurement, can be obtained from the right-hand columns of the three tables by means of: $d = D/10$. For example, for Sample (f) of the limestone, soaked 36 hours, $d = 58.5$ meters. For Sample #66 c) of the granite, soaked 36 hours,

*Cook, J. C., "RF Electrical Properties of Bituminous Coal Samples," Geophysics, v. 35, p. 1079-85 (1970).

Table A - R.F. Electrical Properties of Gran Sasso Limestone

<u>Sample (a) as cut</u>	<u>δ</u>	<u>Z, ohms</u>	<u>κ</u>	<u>ρ, ohm meters</u>	<u>D/2 for 60 dB</u>
1 MHz	24°	10000	7,1	3050	150 meters
5 MHz	15°	2500	5,0	1220	50
25 MHz	7,5°	600	4,0	580	22
100 MHz	1,5°	164	3,7	790	27
<u>Sample (a) Soaked 4 hrs.</u>					
100 MHz	3,5°	170	3,6	350	12
<u>Sample (a) Soaked 16 hrs.</u>					
100 MHz	5,5°	165	3,7	220	8
<u>Sample (b) as cut</u>					
1 MHz	13°	15000	5,0	6000	250
5 MHz	7°	3500	4,8	2580	100
25 MHz	4°	750	4,5	960	37
100 MHz	1°	205	4,1	1060	39
<u>Sample (b) Soaked 4 hrs.</u>					
100 MHz	2°	200	4,2	520	19
<u>Sample (b) Soaked 16 hrs.</u>					
100 MHz	6°	210	3,4	180	6
<u>Sample (c) as cut</u>					
1 MHz	2,5°	19300	3,8	46000	1640
5 MHz	2, °	3800	3,5	11400	390
25 MHz	1,5°	780	3,6	3100	110
100 MHz	1° (?)	210	3,4	1260	42
<u>Sample (d) as cut</u>					
1 MHz	3°	21200	4,1	36500	1350
5 MHz	2°	4300	3,7	11000	380
25 MHz	1°	880	3,15	4500	140
100 MHz	0,5° (?)	242	3,35	2500	85

<u>Sample (e) as cut</u>	<u>δ</u>	<u>Z, ohms</u>	<u>κ</u>	<u>ρ, ohm meters</u>	<u>D/2 for 60 dB</u>
25 MHz	2°	880	3,6	2260	80 meters
100 MHz	1°	200	3,5	1020	35

<u>Sample (f) as cut</u>					
1 MHz	3,5°	16300	5,6	23100	1000
5 MHz	2,5°	3230	5,1	6260	259
25 MHz	2°	690	4,6	1710	67
100 MHz	2°	170	4,7	424	17

<u>Sample (f) Soaked 4 hrs.</u>					
1 MHz	8°	15000	5,6	8360	363
5 MHz	4,5°	3200	5,1	3570	147
25 MHz	2°	680	4,7	1700	67
100 MHz	2°	165	4,8	412	16

<u>Sample (f) Soaked 36 hrs.</u>					
1 MHz	5,5°	15300	5,4	13800	585
5 MHz	3°	3180	5,1	5260	217
25 MHz	2°	650	4,2	1620	60
100 MHz	1,5°	158	5,2	530	22

Table B - R. F. Electrical Properties of St. Gothard Granites

<u>Sample No., Frequency</u>	<u>δ</u>	<u>Z, ohms</u>	<u>κ</u>	<u>ρ, ohm meters</u>	<u>D/2 for 60 dB</u>
#66(a), wet 4 hrs (100 MHz)	0,5°	280	2,4	2200	63 meters
Same, soaked 15 hrs	<0,2°	340	2,6	6700	197
#67(a), wet 4 hrs (100 MHz)	0,5°	295	2,5	2560	74
Same, soaked 15 hrs	<0,2°	290	2,6	6300	186
#68(a), wet 4 hrs (100 MHz)	<0,2°	290	2,5	6300	182
Same, soaked 15 hrs	<0,2°	300	2,3	6500	180

#66(b), dry

1 MHz	1°	19000	2,5	144000	4150
5 MHz	1,2°	3800	2,7	24000	720
25 MHz	0,5°	750	2,5	14200	410
100 MHz	<0,2°	185	2,4	6900	195

Same, soaked 100 hrs

1 MHz	15°	16000	3,0	8200	260
5 MHz	7,3°	3500	2,7	3500	105
25 MHz	2,5°	725	2,6	2150	63
100 MHz	1,2°	175	2,7	1100	33

#66(c), dry

1 MHz	2°	20500	3,0	61200	1940
5 MHz	1,5°	4020	3,08	16200	522
25 MHz	0,7°	820	2,96	7000	220
100 MHz	0,5°	205	2,96	2450	77,4

Same, soaked 36 hrs

1 MHz	16°	17200	3,78	6550	233
5 MHz	5°	3900	3,20	4700	154
25 MHz	1,5°	805	3,06	3220	103
100 MHz	0,5°	200	3,10	2400	77,5

Table C - R.F. Electrical Properties of Washington, D.C. schist

Sample (a), tabular 1.0 x 0.70 x 0.20 inch, f.f. = 0.65

<u>As cut</u>	<u>δ</u>	<u>Z, ohms</u>	<u>r</u>	<u>ρ, ohm meters</u>	<u>D/2 for 60 dB</u>
1 MHz	41.5°	10,000	7.4	1,340	67 meters
5 MHz	20.5°	3,200	5.4	818	35
25 MHz	8.0°	760	4.8	485	20
100 MHz	4.0°	190	4.5	245	9.6

Sample (a),
Soaked 45 hrs

1 MHz	37.5°	11,000	7.1	1,610	79
5 MHz	18°	3,250	5.4	940	40
25 MHz	7.5°	770	4.8	521	21
100 MHz	4.0°	192	4.5	245	9.6

Sample (b), tabular 0.95 x 0.80 x 0.20 inch, f.f. = 0.71

<u>As cut</u>					
1 MHz	19.5°	14,000	6.0	4,050	182
5 MHz	10.5°	3,500	4.8	1,850	75
25 MHz	4.5°	790	4.2	972	37
100 MHz	1.5°	200	3.9	735	27

Sample (b),
Soaked 45 hrs

1 MHz	34°	11,100	6.8	1,920	92
5 MHz	16.5°	3,270	5.1	1,110	46
25 MHz	6.5°	775	4.4	660	26
100 MHz	3.0°	200	3.9	368	13

Sample (c), wedge, 1.2 x 0.9 x 0.10-0.40 inch, f.f. = 0.80

<u>As cut</u>					
1 MHz	18.5°	12,500	4.8	4,200	167
5 MHz	11.5°	3,200	3.9	1,730	62
25 MHz	5.5°	730	3.5	820	28
100 MHz	3.0°	170	3.6	350	12

Sample (c)
Soaked 45 hrs

1 MHz	44.5°	7,400	6.4	1,140	53
5 MHz	24.°	2,550	4.9	672	27
25 MHz	11.°	640	4.1	361	14
100 MHz	4.5°	162	3.8	221	7.9

Notes:

- (1) All samples alike; grey muscovite schist, foliation minor to absent. Very tough.
- (2) Electric field perpendicular to cleavage (foliation) planes in all samples.
- (3) All samples dry-ground to size on SiC wheel.
- (4) Empty-cell 100 MHz impedances: a & b = 437 Ω ; c = 380 Ω .
- (5) Minimum impedances, obtained with wet blotting-paper pads between sample and electrodes and/or with 5 psi compression on foam pads, were used throughout.

Table D - R.F. Electrical Properties of Irondequoit Red Shale

	<u>δ</u>	<u>Z, ohms</u>	<u>κ</u>	<u>ρ, ohm-m</u>	<u>D/2 for 60 dB</u>
<u>Vert. Polariz.</u>					
25 MHz	26°	230	8,3	72	3,8 meters
100 MHz	27,5°	74	5,5	22	0,95
<u>Horiz. Polariz.</u>					
25 MHz	17°	370	8,15	113	5,9
100 MHz	21°	100	6,6	25	1,18

$d = 23.3$ meters. These are very favorable results and show that the practical probing depth of a stress-measuring r.f. magnetic field in such rocks would be limited only by field spreading and coil geometry.

Measurements were not made at 1 MHz in the fresh red shale, but the 25 MHz results, $d = 0.38$ m and $d = 0.59$ m can probably be extrapolated to 1 MHz by multiplying by ten, since the resistivities are comparable to those of grey shale given elsewhere.* The result is a 6 dB propagation distance of the order of 3.5 meters in this shale. Even this would be satisfactory. Shales contain a substantial amount of finely divided feldspar, which might make them candidates for stress-measurements through the nuclear quadrupole resonance of aluminum-27.

*See footnote on page 1.

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REPORT OF INVENTIONS AND SUBCONTRACTS

(Pursuant to "Patent Rights" Contract Clause)

Form Approved

Budget Bureau No. 22-R160

INSTRUCTIONS TO CONTRACTOR

This form may be used for INTERIM and FINAL reports, and when used shall be completed and forwarded to the Contracting Officer in triplicate.

An INTERIM report shall be submitted at least every twelve months, commencing with the date of the contract, and should include only those inventions and subcontracts for which complete information has not previously been reported.

A FINAL report shall be submitted as soon as practicable after the work under the contract is complete and shall include (a) a summary of all inventions required by the contract to be reported, including all inventions previously reported and any inventions since the last INTERIM report, and (b) any required information for subcontracts which has not previously been reported.

1. NAME AND ADDRESS OF CONTRACTOR

Teledyne Geotech
3401 Shiloh Road
Garland, Texas 75040

2. CONTRACT NUMBER

HO220018

3. TYPE OF REPORT (check one)

☐ a. INTERIM ☒ b. FINAL

SECTION I - INVENTIONS ("Subject Inventions" required to be reported by the "Patent Rights" clause)

4. INVENTION DATA (check one)

☒ a. THERE WERE NO INVENTIONS WHICH REASONABLY APPEAR TO BE PATENTABLE

☐ b. LISTED BELOW ARE INVENTIONS WHICH REASONABLY APPEAR TO BE PATENTABLE. ANY INVENTION DISCLOSURES WHICH HAVE NOT BEEN PREVIOUSLY SUBMITTED TO THE CONTRACTING OFFICER ARE ATTACHED TO THIS REPORT

(i) NAME OF INVENTOR	(ii) TITLE OF INVENTION	(iii) PATENT APPLICATION SERIAL NUMBER AND CONTRACTOR'S DOCKET NO.	(iv) CONTRACTOR HAS FILED OR WILL FILE U.S. PATENT APPLICATION		(v) CONFIRMATORY LICENSE OR ASSIGNMENT HAS BEEN FORWARDED TO CONTRACTING OFFICER	
			YES	NO	YES	NO

SECTION II - SUBCONTRACTS (Containing a "Patent Rights" clause)

5. LISTED BELOW IS INFORMATION REQUIRED BUT NOT PREVIOUSLY REPORTED FOR SUBCONTRACTS (If not applicable, write "None")

(i) NAME AND ADDRESS OF SUBCONTRACTOR	(ii) SUBCONTRACT NUMBER	(iii) DATE CLAUSE FURNISHED TO CONTRACTING OFFICER	(iv) DATE SUBCONTRACT COMPLETED
None			

SECTION III - CERTIFICATE

CONTRACTOR CERTIFIES THAT THIS REPORT OF INVENTIONS AND SUBCONTRACTS, INCLUDING ANY ATTACHMENTS, IS CORRECT TO THE BEST OF THE CONTRACTOR'S KNOWLEDGE AND BELIEF

DATE: 12 Jul 1973
NAME AND TITLE OF AUTHORIZED OFFICIAL (Print or Type): J. C. Cook, Principal Geophysicist
SIGNATURE: *John C. Cook*